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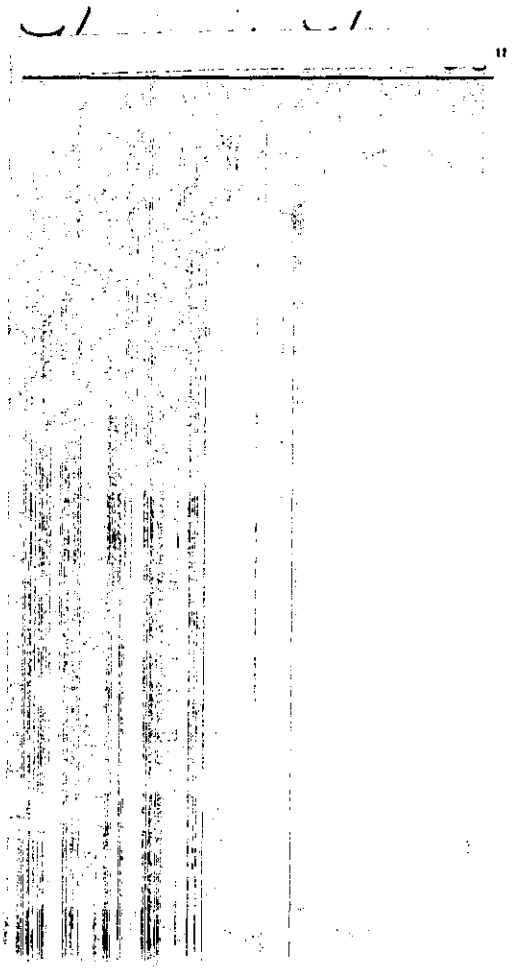

PART ONE

THE MECHANISM OF THE BENZILIC ACID REARRANGEMENT

PART TWO

THE ACTIVITY COEFFICIENTS OF CERTAIN AROMATIC COMPOUNDS

A THESIS

Presented to

the Faculty of the Graduate Division

by

Howard Wayne Haworth

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

in the School of Chemistry

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June, 1962

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PART ONE

The Mechanism of the Benzilic Acid Rearrangement

PART TWO

Activity Coefficients of Certain Aromatic Compounds

Approved: [signature]

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Date approved by Chairman: June 2, 1962

ACKNOWLEDGEMENTS

My most sincere thanks are to be expressed to Dr. Jack Hine whose interest and guidance over a number of years enabled this work to be performed. I acknowledge my gratitude also to the Rayonier Corporation, the National Science Foundation, and the Alfred P. Sloan Foundation for grants that supported the work. Most of all, I gratefully acknowledge the patient understanding and assistance from my wife, without which this work could not have been completed.

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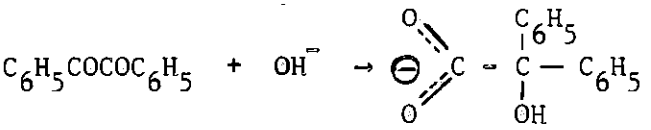
SUMMARY

PART ONE

A number of mechanisms have been proposed for the rearrangement of benzil to benzilic acid in the presence of base. One type of mechanism postulates that the required proton transfer occurs during the rate-controlling step, which may occur simultaneously with base attack or may follow initial attack by the base. In contrast to this, mechanisms have been proposed in which the proton transfer follows a rate-controlling migration of the phenyl group. Regardless of the mechanism, the overall transformation is the following:



It should be possible to learn whether a proton transfer occurs in the rate-controlling step by comparing the rates of base-catalyzed rearrangement in light and heavy water. These rates were determined in the present study.

The rate determinations were made in dioxane-water solution at temperatures near 50°C. The benzil was dissolved in dioxane and allowed to reach bath temperature. Aqueous base, at bath temperature, was added and samples were immediately withdrawn to determine the initial base concentration by titration. Thereafter, the course of the reaction was followed by withdrawing samples at intervals and titrating them with standard hydrochloric acid.

Preliminary experiments with protium oxide and sodium hydroxide gave the approximate rate of rearrangement and showed that this rate was not changed by using sodium hydroxide prepared by reaction of elemental sodium with water, rather than by using carbonate-free sodium hydroxide solution. A solution of sodium deuteroxide in heavy water was prepared by the reaction of elemental sodium with an excess of deuterium oxide. This solution was standardized against hydrochloric acid. The rate of rearrangement catalyzed by sodium deuteroxide in deuterium oxide was measured and found to be faster than the rate of rearrangement catalyzed by sodium hydroxide in protium oxide.

To insure that similar conditions were used in determining relative rates of reaction in light and heavy water, simultaneous runs were made using the same bath and the same reagents. Points from both runs were taken at similar times.

In all cases, it was found that the rearrangement showed second-order kinetics, being first-order in benzil and first-order in base.

From the rate constants for reaction, the k_{H_2O}/k_{D_2O} ratio for the base-catalyzed benzilic acid rearrangement was calculated to be 0.52. Reactions in which bonds to hydrogen are broken in the rate-determining step show primary deuterium kinetic isotope effects that are greater than unity. The smallest reported value for reactions of this type (other than some reactions whose rates may be collision controlled) is 1.3. Reactions involving proton transfers in steps other than the rate-controlling step show k_{H_2O}/k_{D_2O} ratios less than unity, due to the increased basicity of deuteroxide ion in deuterium oxide compared to

hydroxide ion in protium oxide. The k_{H_2O}/k_{D_2O} ratio of 0.52 observed in the present study is among the lowest reported.

The possibility that the k_{H_2O}/k_{D_2O} ratio included a primary kinetic isotope effect compensated by the secondary kinetic isotope effect is quite small. To include a primary kinetic effect of 1.3 (a minimum value) the secondary solvent isotope effect would be required to be 0.41, a value lower than any previously reported. Hence this possibility is considered to be unlikely, and the proton transfer in the rate-controlling step that would be responsible for a primary deuterium kinetic isotope effect is considered extremely improbable.

PART TWO

For many years, an empirical equation called the Hammett equation has been used to correlate relative equilibrium constants for a variety of organic reactions such as the reaction series $ArX_1 \rightleftharpoons ArX_2$. The terms X_1 and X_2 represent different groups, such as $-CO_2H$, $-Br$, $-SO_3H$, etc. Relative equilibrium constants can be expressed by the equation $\log (K_Y^X/K_o^X) = \rho_X\sigma_Y$. The term K_o^X is the equilibrium constant for the reaction of the unsubstituted compound, and K_Y^X is the equilibrium constant for the reaction of the compound with a meta or para substituent Y. The term ρ_X is dependent upon the type of reaction that changes X_1 to X_2, and σ_Y is a constant characteristic of the meta or para Y substituent. This equation is limited in that it applies only to either meta or para substituents and not to ortho substituents. Thus it is not applicable to all aromatic compounds.

It has recently been shown that it does not apply to all meta and para substituted compounds since ρ is required to be the same for both cases. A modification of this equation has been proposed in which the ρ term is taken to be proportional to a difference in σ values for X_1 and X_2. The proportionality constant can be expressed in terms of a constant, τ, which measures the transmittance of the effect of a meta or para substituent to the reaction site. The tau values for meta and para substituents are not required to be equal. The value of tau should be constant for a given set of reaction conditions, but could vary with temperature, ionic strength, and the nature and dielectric constant of any

solvents. For the reaction series

$$\underline{p}\text{-}Y_1C_6H_4X_1 \rightleftarrows \underline{p}\text{-}Y_1C_6H_4X_2$$
$$\underline{p}\text{-}Y_2C_6H_4X_1 \rightleftarrows \underline{p}\text{-}Y_2C_6H_4X_2$$

it can be shown that

$$\log \frac{K_{\underline{p}\text{-}Y_1}}{K_{\underline{p}\text{-}Y_2}} = \tau_{\underline{p}}(\sigma_{\underline{p}\text{-}Y_1} - \sigma_{\underline{p}\text{-}Y_2})(\sigma_{\underline{p}\text{-}X_1} - \sigma_{\underline{p}\text{-}X_2})$$

The term $\underline{p}$-Y refers to a Y substituent in a position <u>para</u> to the reaction site, and $\sigma_{\underline{p}}$ is the substituent constant for substituent located <u>para</u> to the other group present. The term $\tau_{\underline{p}}$ is the <u>tau</u> value for groups located <u>para</u> to each other. A similar expression can be written for the <u>meta</u> case. For disproportionation reactions of the type $2C_6H_5X \rightleftarrows C_6H_6 + C_6H_4X_2$, it has been shown that if the activity coefficients of the compounds in solvent B are determined with reference to another solvent A,

then $\log \frac{f_{Ph}^{B} f_{PhX_2}^{B}}{(f_{PhX}^{B})^2} = (\tau^A - \tau^B)(\sigma_X)^2$. The term f_C^B is the activity coefficient for compound C in solvent B with reference to solvent A. This work was performed to test the validity of the above equation.

The activity coefficients of benzene, bromobenzene, <u>m</u> and <u>p</u>-dibromobenzene, nitrobenzene, and <u>m</u> and <u>p</u>-dinitrobenzene were determined in decalin with reference to the vapor state, and in water with reference to the vapor state.

The vapor pressures of the various materials as pure substances

or saturated solutions in decalin were measured and the partial pressures of solutions in decalin of known concentrations were determined. Known amounts of nitrogen were saturated with organic vapor in a saturator immersed in a constant temperature bath. The organic vapors were then condensed and the amounts of organic materials present were determined by weighing or by analyzing through use of their ultraviolet absorption spectra. The solubilities of these materials in decalin were determined and their solubilities in water were known from earlier work. If the gaseous state is taken as the reference state the activity coefficients in decalin solution with reference to the vapor state can be calculated by dividing the partial pressure of the substance in a decalin solution of known concentration by the concentration of the solution. The activity coefficient of a substance in water with reference to the vapor state can be obtained by dividing the vapor pressure of the pure material by the concentration of a saturated solution in water.

Plots of the term $\log \frac{f_{PhX}\, f_{PhX_2}}{(f_{PhX})^2}$ <u>vs.</u> σ_x^2 were made from activity coefficients calculated in the above manner. This should yield a straight line, passing through the origin, whose slope was the difference in <u>tau</u> values for the two media being considered. It was found that agreement was observed in all but one case, where the complication of solvent-solute interaction may exist. The <u>tau</u> differences between media were found to be no larger than the uncertainty of the value in aqueous solution.

The activity coefficient ratios found in the present work, being numbers greater than unity, indicate that separation of groups by locating them in meta and para positions on a benzene ring does not separate them sufficiently to be independent of each other. Were this the case, the activity coefficient ratios would be unity. These differences from unity are correlated with reasonable accuracy by the above equations.

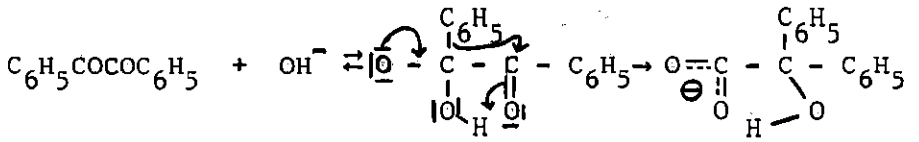
PART ONE

THE MECHANISM OF THE BENZILIC ACID REARRANGEMENT

CHAPTER I

INTRODUCTION

A number of investigators (1) have proposed that the mechanism for the rearrangement of benzil to benzilic acid in the presence of base involves the migration of a phenyl group accompanied by the migration of an oxygen-bound hydrogen atom.



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Ott and Smith (2) proposed a concerted mechanism where base attack causes the formation of benzilic acid in one step without the formation of intermediates such as I. The concerted mechanism has been shown to be improbable by the report of Roberts and Urey (3) that benzil undergoes a base-catalyzed O^{18} exchange. Arguments that proton transfer must be a part of the rate-controlling step because of the lack of similar products from the reaction of benzil and alkoxide ions have been discounted by the work of Doering and Urban (4). They have also shown that sodium methoxide and

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1. A. Michael, J. Am. Chem. Soc., 42, 787 (1920); M. T. Clark, E. C. Hendley, and O. K. Neville, ibid., 77, 3280 (1955).

2. D. G. Ott and G. C. Smith, ibid., 77, 2325 (1955).

3. I. Roberts and H. C. Urey, ibid., 60, 880 (1938).

4. W. v. E. Doering and R. S. Urban, ibid., 78, 5938 (1956).

potassium t-butoxide do give the corresponding benzilic acid esters, and the reaction of benzil with sodium ethoxide is complicated by hydride ion transfer.

In order to gain further insight into the proton transfer step, it was decided to investigate the deuterium kinetic isotope effect.

Chapter II

EXPERIMENTAL

Equipment Used

The first kinetic runs were made in glass flasks. When it became apparent that there was considerable attack on the glass by the base used, a change was made and polyethylene bottles with rubber stoppers were used for the remainder of the runs.

The reactants were kept at a constant temperature by the use of a water-filled constant temperature bath. The temperature of the bath was determined by the use of a thermometer calibrated by the United States Bureau of Standards. It was desired that all runs be performed at 50°C, but in later runs, the temperature was as low as 49.5°C. The runs using deuterium oxide and sodium deuteroxide were made simultaneously with runs using protium oxide and sodium hydroxide and the temperature did not vary within such runs. Thus a valid comparison of reaction rates was obtained.

Procedure

Preparation for a Run.--The benzil on hand, after recrystallization from ethanol, was dissolved in benzene and washed with an aqueous solution of base. The benzene solution was then washed with water and evaporated until crystallization began. Cooling brought crystals

(m.p. 96.0-96.5°C[1], uncalibrated thermometer) that were filtered and stored in a desiccator over calcium chloride. The material still appeared to contain approximately one per cent of an acidic impurity. The impurity could not be removed by repeating the base wash and filtration under an atmosphere of dry nitrogen.

The dioxane used was purified by the method of Fieser. (6)

The base used was prepared in several fashions. Early runs used carbonate-free sodium hydroxide solution standardized against hydrochloric acid to the phenolphthalein end point. Later, when runs were made simultaneously in light and heavy water, the base solutions used were prepared by the reaction of metallic sodium with protium oxide and deuterium oxide. Each was standardized with the same hydrochloric acid solution to the phenolphthalein end point.

The polyethylene bottle used was just large enough to accomodate the reactants. When a considerably larger bottle was used, loss of solvent, apparently mostly dioxane, caused the separation of a solid material after the first few points were taken. This was accompanied by a rise in the rate constant. With the smaller bottle, however, the solution remained clear until near the end of the reaction, and no

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[1] The literature value for the m.p. of benzil is 95°C (5).

5. N. A. Lange, Handbook of Chemistry, 7th ed., Handbook Publishers, Inc., Sandusky, Ohio, 1949, p. 386.

6. L. F. Fieser, Experiments in Organic Chemistry, 3rd ed., D. C. Heath and Co., Boston, Massachusetts, 1955, p. 285.

corresponding rise in the rate constant was observed. Only in the first determination of the rate constant at 50°C was a measurement from a non-homogeneous solution used to calculate the average value for the rate constant.

Description of a Typical Run.--Eighty milliliters of dioxane was pipetted under nitrogen into the bottle which already contained a weighed amount of benzil. The bottle was placed in the constant temperature bath and allowed to reach bath temperature. After about twenty minutes, 40 ml. of the base, at bath temperature, was pipetted into the bottle and the contents shaken thoroughly. Two ten-milliliter samples were then withdrawn and pipetted into cold acetone. This served to stop further reaction and served as a cosolvent to keep the unreacted benzil in solution during titration. The samples were then titrated with standard hydrochloric acid within five minutes. The average titer of the two samples was taken as the zero time titer for the base present, and the average time of withdrawal as the zero time for the reaction.

Thereafter, ten-milliliter samples were withdrawn at various intervals of time and treated in similar fashion. In general, samples were withdrawn while a stream of nitrogen was passed over the reaction bottle. In the cases where this was not done, however, no difference in rate constant was observed.

In order to calculate the concentration of benzil correctly it was necessary to determine the expansion of the dioxane while reaching bath temperature and the decrease in total volume when dioxane and the aqueous base were mixed. A blank was run on the dioxane and base with

no benzil present. A mixture of 80 ml. of dioxane and 40 ml. of 0.1128 N sodium hydroxide was allowed to reach bath temperature. Two 15 ml. samples were withdrawn and pipetted into 10 ml. samples of cold acetone. These were then titrated with 0.1246 N hydrochloric acid, and required 4.39 ml. and 4.41 ml. for neutralization to the phenolphthalein end point. The average titer was 4.40 ml. A titer of 4.53 ml. was calculated on the basis of the assumption that there is no change in the total volume either when the aqueous solution and dioxane are mixed or when the mixture is heated. Thus a mixture of 80 ml. of dioxane and 40 ml. of base give a volume of 120.0 x (4.53/4.40) = 123.5 ml. at 50°C. The concentration of benzil at zero time was calculated in the following way. In a typical run, 1.6830 grams of benzil (mol. wt. = 210.2) was weighed into a bottle and the dioxane and base added. The volume of the solid benzil was 1.6830 g./1.23 g./ml. = 1.37 ml. Assuming the volume of the solution increased by that amount, the original concentration of benzil was (1.6830/210.2) x [1000/(123.5 + 1.37)] = 0.0641 M.

This benzil concentration was further corrected for the acid impurity and reaction before zero time. The 0.1246 M acid titer (no benzil present) was 4.40 ml. x (120.0/121.37) = 4.35 ml. Subtracting the zero time titer value of 4.16 ml. from this gives a change in acid titer due to reaction or impurity of 0.192 ml. The 0.192 ml. of 0.1246 N acid contains 0.0239 meq. of acid, which in 121.37 ml. of solution would result in a concentration change of 0.0002 M. The corrected benzil concentration is 0.0641 M -0.0002 M = 0.0639 M. In no case was the total correction more than four per cent.

CHAPTER III

RESULTS

Summary of Results.--The data for individual runs are given in the appendix. All previous work indicates the reaction follows second-order kinetics, being first-order in benzil and first-order in base. In such a case, k, the second-order rate constant is given by the equation

$$k = \frac{1}{t(a - b)} \ln \frac{b(a - x)}{a(b - x)}$$

where a and b are the molar concentrations of reactants at zero time, t is the time elapsed since the zero time was determined, and (a - x) and (b - x) are the concentrations of the reactants at time t. The value of x was found by subtracting the number of milliequivalents of base at time t from the number found at zero time and dividing by the volume of the sample. Values of k so calculated are given in the third column of each table in the appendix. The results of the various runs are given in Table 1.

Discussion of Simultaneous Runs.--The most conclusive determinations were obtained by making simultaneous runs in light and heavy water. These were the runs made at 49.5°C and 49.8°C shown in Table 1. The benzil used in these cases was obtained from the same container after the solid had been thoroughly mixed to insure that identical samples could be obtained. During the runs, samples were taken from

Table 1

Reaction of Benzil with Alkali in 66 2/3 per cent Dioxane - 33 1/3 per cent Water by Volume

Temp., °C	Water used	k x 10 l. mole^{-1} hr.$^{-1}$	k x 10^5 l. mole^{-1} sec.$^{-1}$
49.5°C	D_2O	5.369 ± 0.028	14.91 ± 0.08
49.5°C	H_2O	2.915 ± 0.033	8.11 ± 0.10
49.8°C	D_2O	5.840 ± 0.011	16.22 ± 0.03
49.8°C	H_2O	3.127 ± 0.007	8.67 ± 0.02
50°C[a]	H_2O	3.501 ± 0.087	9.72 ± 0.24
50°C	H_2O	3.613 ± 0.123	10.04 ± 0.35
50°C	H_2O	3.592 ± 0.114	9.98 ± 0.32
50.6°C	D_2O	6.761 ± 0.187	18.78 ± 0.52

[a] This run used 60 per cent dioxane–40 per cent water as a solvent.

both reaction vessels and titrated at virtually the same time except for the first point of the deuterium system. Because of the faster rate of reaction in heavy water, determinations were begun on the runs in heavy water before they were begun on the runs in light water. The same hydrochloric acid was used for both titrations which were made without refilling the buret.

Difficulty was encountered in regulation of the bath temperature. Although the temperature did not vary within a run, it did vary from one run to another, and variations in rate constants were encountered. However, since the protium and deuterium runs were made simultaneously, a valid comparison of rate constants is possible, regardless of the actual temperature of the run.

Determination of Solvent Effect.--The reaction rate was measured in a somewhat different solvent mixture 60 per cent dioxane-40 per cent water to determine whether the differences observed in the reaction rates in light and heavy water could be due to differences in molal volume of deuterium and protium oxide or due to small amounts of differential evaporation. The solvent effect is shown not to be large since reaction rates in 60 per cent dioxane and 66 2/3 per cent dioxane differ by less than three per cent.

Application of Results.--From the results of the present work, it seems improbable that the benzilic acid rearrangement involves a proton transfer in the rate-controlling step. The most probable mechanism is one suggested by Ingold (7) in which the migration of the phenyl group is

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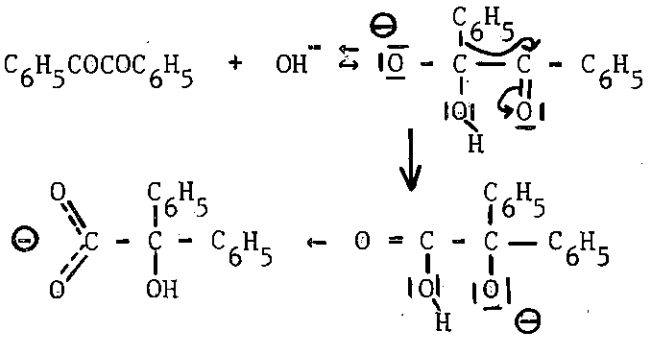
7. C. K. Ingold, Ann. Rept. Chem. Soc., 25, 124 (1928); 30, 177 (1933).

the rate controlling step. The proton transfer follows this step.



Since the rate of rearrangement in deuterium oxide-sodium deuteroxide is almost twice as fast as in protium oxide-sodium hydroxide it seems improbable that an oxygen-hydrogen bond is broken in the rate controlling step. Westheimer (8) gives considerable data about primary deuterium kinetic isotope effects. All of these data give k_H/k_D ratios that are greater than unity, with the smallest example cited (other than those found in certain processes such as the reaction of a Grignard reaction with an alcohol that may be diffusion controlled) being 1.3.

The k_H/k_D ratio is in accord with a number of examples of the greater basicity of deuteroxide ions over hydroxide ions. This secondary isotope effect is shown in two types of reaction. Ballinger and Long (9) have found that in the reaction of base with ethylene chlorohydrin, $k_H/k_D = 0.84$. This illustrates reactions in which the base serves to remove a proton from a Brønsted acid. The base catalyzed hydrolysis of

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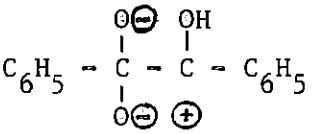
8. F. H. Westheimer, Chem. Revs., 61, 265 (1961).

9. P. Ballinger and F. A. Long, J. Am. Chem. Soc., 81, 2347 (1959).

esters is similar to the benzilic acid rearrangement in that base attack involves the displacement of an electron pair toward a carbonyl oxygen. Bunton and Shiner (10) cite k_{H_2O}/k_{D_2O} values of 0.63, 0.73, and 0.50 for the alkaline hydrolysis of ethyl acetate, ethyl formate, and t-butyl acetate, respectively.

The k_H/k_D ratio of 0.54 obtained in the base-catalyzed benzilic acid rearrangement renders extremely unlikely the possibility that the rate controlling step involves a proton transfer. It does not rule it out entirely. However, the k_H/k_D ratio of 0.54 is already among the lowest value reported. If this were due to a secondary isotope effect partially compensated for by a small primary isotope effect, the secondary isotope effect would be required to be even larger. If the smallest reported primary isotope effect of 1.3 (8) were applied to the k_H/k_D ratio of 0.54 obtained here, it would require that the secondary isotope effect be 0.41. This is lower than any value so far reported. Thus it is seen that the presence of a primary kinetic isotope effect is ruled very unlikely, and therefore a proton transfer in the rate controlling step is also unlikely.

The observed rate difference does not rule out the possibility of an intermediate such as



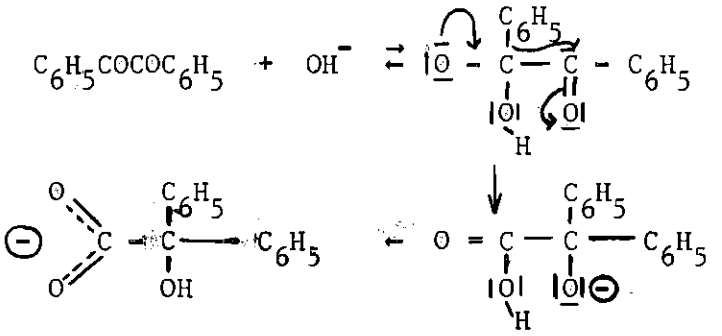
10. C. A. Bunton and V. J. Shiner, ibid., 83, 3207 (1961).

which could be in equilibrium with the reactants. The possibility of this as an intermediate is shown to be small by Doering and Urban (4) who found that the reaction of benzil with sodium methoxide or potassium t-butoxide gives the corresponding benzilic acid esters.

CHAPTER IV

CONCLUSION

The mechanism for the base-catalyzed benzilic acid rearrangement that was proposed by Ingold (7)



is supported by the observed ratio of rates of reaction in light and heavy water.

Mechanisms that involve proton transfer in the rate-controlling step are shown to be quite improbable by the apparent lack of primary deuterium kinetic isotope effect.

APPENDIX

Table 2

Reaction of Benzil with Sodium Hydroxide in 66 2/3 per cent Dioxane - 33 1/3 per cent Water at 50°C.

$[Benzil]_o = 0.05304$		$[NaOH]_o = 0.03396$
time, hrs.	[NaOH]	k x 10 l. $mole^{-1}$ $hr.^{-1}$
17.0	0.02567	3.384
21.77	0.02335	3.636
25.75	0.02157	3.843
28.05	0.02051	3.697
41.85	0.01749	3.656
66.55	0.01340	3.462
		Av. 3.613 ± 0.123
$[Benzil]_o = 0.04911$		$[NaOH]_o = 0.03247$
time, hrs.	[NaOH]	k x 10 l. $mole^{-1}$ $hr.^{-1}$
22.7	0.02296	3.493
31.92	0.01972	3.729
44.68	0.01752	3.417
51.33	0.01549	3.694
69.33	0.01305	3.522
77.18	0.01164	3.694
		Av. 3.592 ± 0.114

Table 3

Reaction of Benzil with Sodium Deuteroxide in 66 2/3 per cent Dioxane - 33 1/3 per cent Deuterium Oxide at 50.6°C

$[Benzil]_o$ = 0.05340 $[NaOD]_o$ = 0.04234

time, hrs.	[NaOD]	k x 10 l. $mole^{-1}$ $hr.^{-1}$
18.25	0.02424	7.097
29.45	0.01929	6.778
42.25	0.01600	6.988
48.05	0.01401	6.573
53.55	0.01297	6.454
66.50	0.01040	6.694
		Av. 6.761 ± 0.187

Table 4

Reaction of Benzil with Alkali in 66 2/3 per cent Dioxane - 33 1/3 per cent Water. Simultaneous Runs at 49.5°C.

$[Benzil]_o$ = 0.06639		$[NaOD]_o$ = 0.04278	
water used	time, hrs.	[NaOD]	k x 10 1. $mole^{-1}$ $hr.^{-1}$
D_2O	9.67	0.03117	5.367
D_2O	21.4	0.02270	5.419
D_2O	27.5	0.01963	5.401
D_2O	45.83	0.01335	5.350
D_2O	51.25	0.01206	5.331
D_2O	54.94	0.01122	5.344
			Av. 5.369 ± 0.028

$[Benzil]_o$ = 0.05686		$[NaOH]_o$ = 0.03201	
water used	time, hrs.	[NaOH]	k x 10 1. $mole^{-1}$ $hr.^{-1}$
H_2O	22.31	0.02283	2.923
H_2O	28.28	0.02083	2.992
H_2O	46.42	0.01678	2.899
H_2O	52.31	0.01640	2.908
H_2O	55.94	0.01514	2.854
			Av. 2.915 ± 0.033

Reactions at 49.8°C.--Simultaneous runs were made at this temperature for the purpose of checking the first pair of simultaneous runs. Only two points were taken for each. The average rate constants are shown below, but the primary data have been lost.

$$k_{D_2O} \times 10 \text{ l. mole}^{-1} \text{ hr.}^{-1} = 5.840 \pm 0.011$$

$$k_{H_2O} \times 10 \text{ l. mole}^{-1} \text{ hr.}^{-1} = 3.127 \pm 0.007$$

Table 5

Reaction of Benzil with Sodium Hydroxide in 60 per cent Dioxane - 40 per cent Water at 50°C

$[Benzil]_o = 0.03841$	$[NaOH]_o = 0.03808$	
time, hrs.	[NaOH]	k x 10 l. $mole^{-1}$ $hr.^{-1}$
23.55	0.02904	3.467
43.0	0.02464	3.358
45.62	0.02358	3.641
47.08	0.02350	3.528
47.95	0.02323	3.595
48.63	0.02252	3.416
		Av. 3.501 ± 0.087

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2. D. G. Ott and G. G. Smith, ibid., 77, 2325 (1955).

3. I. Roberts and H. C. Urey, ibid., 60, 880 (1938).

4. W. v. E. Doering and R. S. Urban, ibid., 78, 5938 (1956).

5. N. A. Lange, Handbook of Chemistry, 7th ed., Handbook Publishers, Inc., Sandusky, Ohio, 1949, p. 386.

6. L. F. Fieser, Experiments in Organic Chemistry, 3rd ed., D. C. Heath and Company, Boston, Massachusetts, 1955, p. 285.

7. C. K. Ingold, Annual Reports of the Chemical Society, 25, 124 (1928); 30, 177 (1933).

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PART TWO

ACTIVITY COEFFICIENTS OF CERTAIN AROMATIC COMPOUNDS

CHAPTER I

INTRODUCTION

An equation proposed by Hammett (1) has long been used to predict relative equilibrium constants. It is applicable to series of the type

$$C_6H_5X_1 \overset{K_o^X}{\rightleftharpoons} C_6H_5X_2$$

$$\underline{m} \text{ or } \underline{p}\text{-}YC_6H_4X_1 \overset{K_Y^X}{\rightleftharpoons} \underline{m} \text{ or } \underline{p}\text{-}YC_6H_4X_2$$

The ionization of benzoic acids, $C_6H_5CO_2H \rightleftarrows C_6H_5CO_2^- + H^+$, is an example in which X_1 is $-CO_2H$ and X_2 is $-CO_2^-$. The term K_o^X is the rate or equilibrium constant for the reaction of an unsubstituted compound, K_Y^X is the rate or equilibrium constant for a compound with a meta or para Y substituent under the same conditions. According to the Hammett equation the relative equilibrium constants may be expressed as $\log (K_Y^X/K_o^X) = \rho_X\sigma_Y$, where ρ_X is a constant dependent upon the nature of the reaction, the solvent and the temperature, and σ_Y is a constant determined by the nature of the meta or para Y substituent. The equation is limited by the assumption that ρ_X must be the same, regardless of whether meta or para substituents are present, although

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1. L. P. Hammett, Physical Organic Chemistry, McGraw-Hill Book Company, Inc., New York, N. Y., 1940, p. 184; Chem. Revs., 17, 125 (1935); J. Am. Chem. Soc., 59, 96 (1937).

meta and para σ values are not required to be the same.

Hine (2) has shown that this limitation causes the Hammett equation to be unsuitable for meta and para substituted derivatives in general. He proposes that the ρ value is proportional to the differences in σ values for the two groups X_1 and X_2, and the proportionality constant can be expressed in terms of another constant tau which is dependent only on reaction conditions. Tau measures the effectiveness with which the influence of the substituent is transmitted through the benzene ring to the site of reaction. While tau will have a definite value for specific conditions, it may vary with the temperature, ionic strength, and the nature and dielectric constant of the solvent. The tau values for reactions of meta and para substituted compounds are not required to be equal. Thus for a reaction series

$$\underline{p}\text{-}Y_1C_6H_4X_1 \rightleftarrows \underline{p}\text{-}Y_1C_6H_4X_2$$
$$\underline{p}\text{-}Y_2C_6H_4X_1 \rightleftarrows \underline{p}\text{-}Y_2C_6H_4X_2$$

the Hammett equation would predict the following

$$\log \frac{K^X_{\underline{p}\text{-}Y_1}}{K^X_{\underline{p}\text{-}Y_2}} = \rho_X(\sigma_{\underline{p}\text{-}Y_1} - \sigma_{\underline{p}\text{-}Y_2})$$

The terms $\underline{p}\text{-}Y_1$ and $\underline{p}\text{-}Y_2$ refer to substituents Y_1 and Y_2 on the benzene ring in positions para to the X groups, and $\sigma_{\underline{p}\text{-}Y}$ is the substituent constant for the group Y in that position. The term ρ_X is the constant

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2. J. Hine, ibid., 81, 1126 (1959).

for the reaction that changes X_1 to X_2, and $K^X_{\underline{p}\text{-}Y}$ is the equilibrium constant for a $\underline{p}$-Y substituted compound undergoing that reaction. In the series

$$\underline{p}\text{-}O_2NC_6H_4CO_2H \rightleftarrows \underline{p}\text{-}O_2NC_6H_4CO_2^- + H^+$$

$$\underline{p}\text{-}BrC_6H_4CO_2H \rightleftarrows \underline{p}\text{-}BrC_6H_4CO_2^- + H^+$$

X_1 is $-CO_2H$, X_2 is $-CO_2^-$, Y_1 is $-NO_2$, and Y_2 is -Br. Hine states that the term ρ_X can be expressed as $\rho_X = \tau_{\underline{p}}(\sigma_{\underline{p}\text{-}X_1} - \sigma_{\underline{p}\text{-}X_2})$ and the overall expression as the following:

$$\log \frac{K^X_{\underline{p}\text{-}Y_1}}{K^X_{\underline{p}\text{-}Y_2}} = \tau_{\underline{p}}(\sigma_{\underline{p}\text{-}Y_1} - \sigma_{\underline{p}\text{-}Y_2})(\sigma_{\underline{p}\text{-}X_1} - \sigma_{\underline{p}\text{-}X_2})$$

The term $\tau_{\underline{p}}$ measures the transmittance of effect from a <u>para</u> substituent to the reaction center, and $\sigma_{\underline{p}\text{-}X}$ is the substituent constant for an X group located in the <u>para</u> position. Other terms are as defined above. A similar expression can be written for the case of <u>meta</u> substituents.

Other applications have been proposed by Hine (3) for these same concepts. For a disporportionation reaction $2C_6H_5X \xrightleftharpoons{K_d^A} C_6H_6 + \underline{p}\text{-}C_6H_4X_2$ in a solvent A, the expression

$$-\log 6\, K_d^A = \tau_{\underline{p}}(\sigma_{\underline{p}\text{-}X})^2$$

may be written. The number 6 is a statistical factor to account for the two possible modes of forward reaction and the twelve possible

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3. J. Hine, <u>ibid.</u>, <u>82</u>, 4877 (1960).

modes of reverse reaction. The thermodynamic equilibrium constant K_d^A can be determined by carrying out the reaction in solutions sufficiently dilute that the activity coefficients are unity. Using a second solvent B, a similar expression can be written for K_d^B. If all the activities are expressed with respect to solvent A as a standard, K_d^A and K_d^B are related by

$$K_d^B = \frac{f_{PhH}^B \, f_{p\text{-}PhX_2}^B}{(f_{PhX}^B)^2} K_d^A$$

where f_C^B represents the activity coefficient of some compound C in solvent B. By combining equations, the expression

$$\log \frac{f_{PhH}^B \, f_{p\text{-}PhX_2}^B}{(f_{PhX}^B)^2} = (\tau_p^A - \tau_p^B)(\sigma_{p\text{-}X})^2$$

is obtained. The terms τ_p^A and τ_p^B are the tau values for para compounds in solvents A and B, and $\sigma_{p\text{-}X}$ is the substituent constant for the group X located in a position para to the reaction site. Similar expressions can be written for the case of meta substituents.

Differences in τ values can be calculated from the above equation if the activity coefficients and σ values are known. The present work was an attempt to determine the activity coefficients, f_C^B, by vapor pressure measurements for a number of aromatic compounds and to test the validity of the above expression. In the present study water and decalin were used as solvents. Water was chosen as a solvent with a high

dielectric constant, and decalin as a solvent with a low dielectric constant. Tau differences could be obtained from the activity coefficients. From the tau differences between water and the vapor state and decalin and the vapor state, attempts were to be made to test the validity of the Hammett equation and the applicability of the proceeding equations to measure the effect of solvents in the transmission of substituent effects.

CHAPTER II

EQUIPMENT

Description of Equipment for Vapor Pressure Measurement

The saturator consists of six pairs of parallel tubes. As shown in Fig. 1, each of these tubes is approximately thirty centimeters in length and two centimeters in diameter. Each tube is connected to the other member of the pair by an inverted U-tube at one end and an inverted Y-tube at the other. The third arm of the "Y" is fitted with a ground glass joint and stopper which can be withdrawn for introduction of a sample or for cleaning. Each pair of tubes is connected from the middle of the second tube to the succeeding pair by a short length of glass tubing that ends with a ground glass ball joint. This joint fits into a ground glass socket joint connected to the middle of the first member of the succeeding pair. By means of these joints, the pairs of tubes can be separated for cleaning and drying. The first tube of the series is equipped with an inlet tube through which nitrogen is introduced into the saturator. The last tube is provided with an exit tube that leads to a trap used for condensing organic vapors. This exit tube is wrapped in heating tape and kept at approximately 40°C to prevent condensation of any vapors as they leave the saturator. The relative positions of saturator, exit tube, and trap are shown in Fig. 2. The saturator is clamped in an aluminum rack that holds the tubes in place, and enables the saturator to be held in a constant temperature bath. The rack is also connected by an

aluminum strip to a motor-driven eccentric gear that serves to rock the saturator through an angle of approximately fifteen degrees. This is illustrated in Fig. 2.

The trap to condense the organic vapors from the saturator is approximately ten centimeters long and 2.5 centimeters in diameter. It is fastened by means of a ball and socket joint to the exit tube from the saturator and held in a Dewar flask on the top of the rack. The exit tube from the trap leads to a "Precision" wet test meter[1] that serves to measure the volume of nitrogen that has passed through the system. This meter is provided with a thermometer so that the temperature at which the nitrogen is measured can be determined. The nitrogen flow through the entire system is shown in Fig. 3.

Methods of measuring vapor pressures that are similar to the one described below are not new. Washburn and Heuse (4) devised a similar apparatus to avoid the errors inherent in the static methods of vapor pressure measurement. Bacarella, Finch, and Grunwald (5) modified this apparatus into one that closely resembles the apparatus described in the present work. These authors, however, made runs through several saturator trains in series, did not employ a heated exit tube, and did not use a meter to measure nitrogen flow.

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[1] Made by Precision Scientific Co., Chicago, Ill.

4. E. W. Washburn and E. O. Heuse, ibid., 37, 309 (1915).

5. A. L. Bacarella, A. Finch, and E. Grunwald, J. Phys. Chem., 60, 573 (1956).

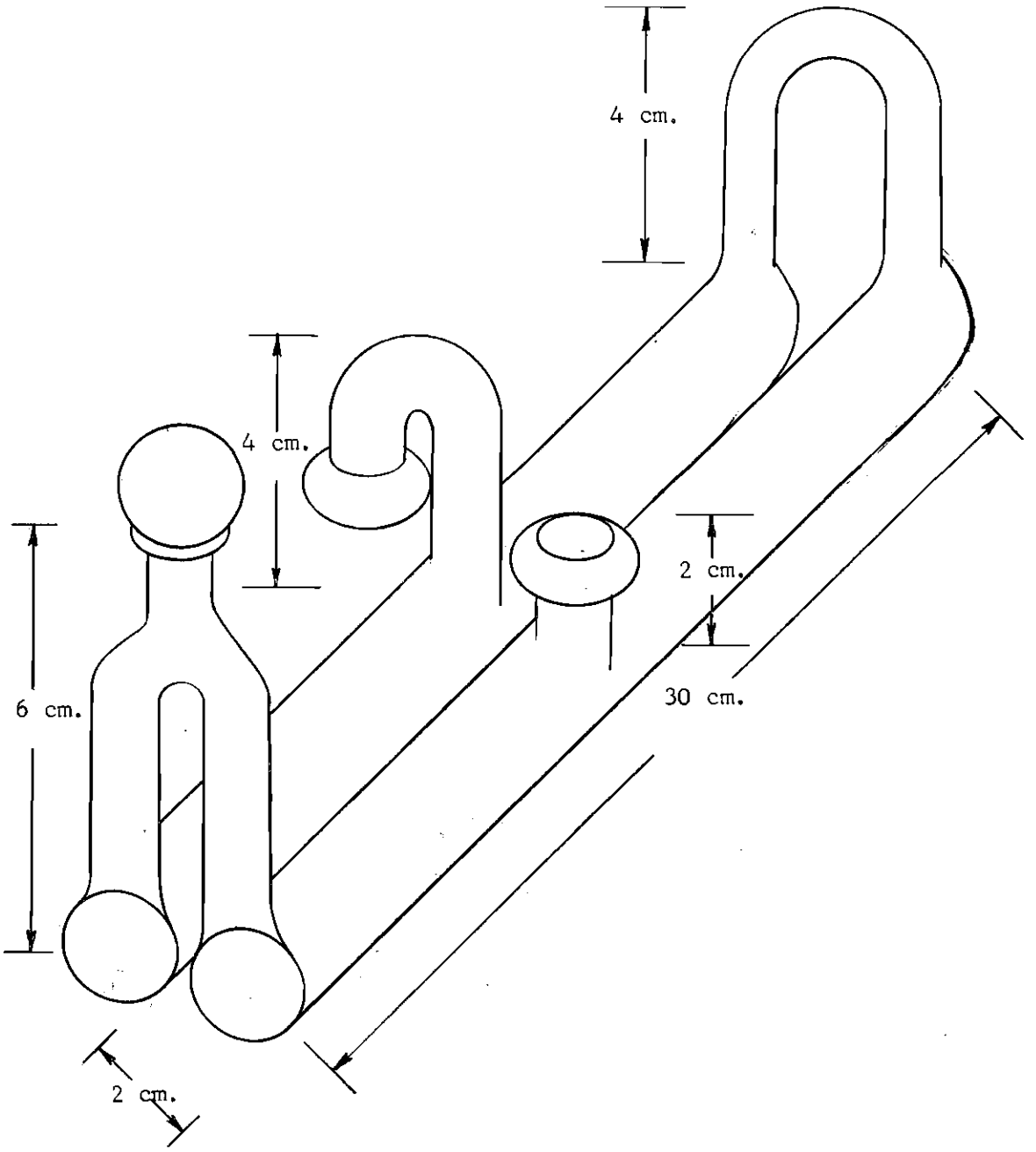

Fig. 1. Diagram of a Pair of Saturator Tubes.

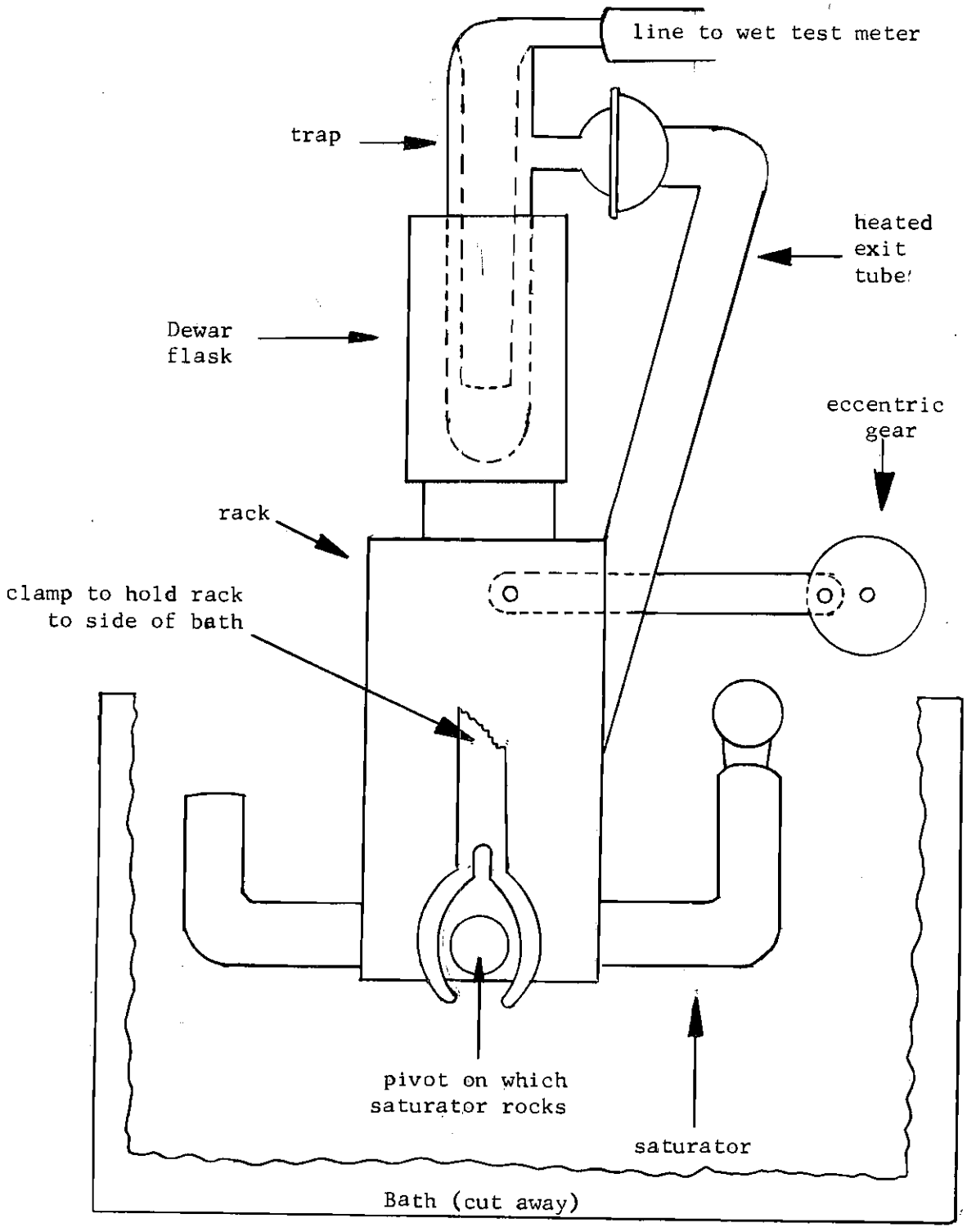

Fig. 2. Cross Section of Apparatus in Bath

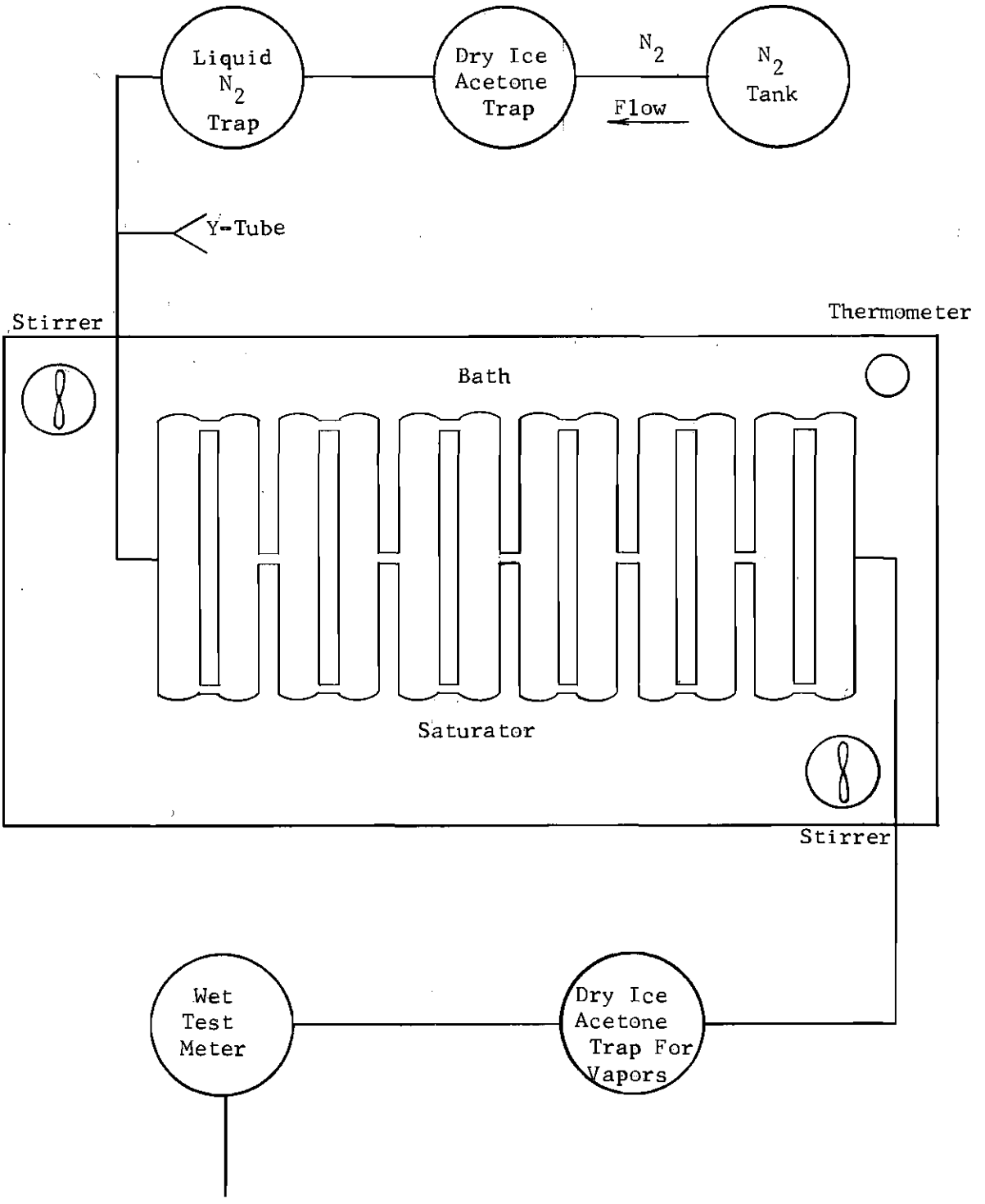

Fig. 3. Diagram of Nitrogen Flow Through the System

Accuracy of Equipment

Temperature of the Bath.--The temperature of the constant temperature bath was measured with a thermometer standardized by the United States Bureau of Standards. The observed reading was 35.1°C. The thermometer used was certified to be accurate at 50°C but to be 0.1°C high at 0°C. It was thought that the bath temperature deviated less than 0.05°C from the desired 35°C.

Variations in temperature throughout the bath were measured by means of a Beckmann thermometer. Readings were taken at several locations and several depths in the bath. It was observed that the maximum variation throughout the bath was 0.07°C and at any one point was 0.05°C. The temperature variation at any one point during one day was constant, and the variation of the maximum temperature during three days at the same point was 0.03°C.

Calculations based upon the vapor pressure of decalin indicated that an error of only 0.39 per cent would be produced if the bath temperature changed 0.1°C.

Accuracy of the Vapor Pressure Measurements.--The determination of the vapor pressure of benzene was chosen as a measure of the accuracy of the apparatus. Several values of the vapor pressure of benzene at a temperature near 35°C are available in the literature. Willingham et al (6) report values that give a vapor pressure of 147.5 mm. when

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6. C. B. Willingham, W. J. Taylor, J. M. Pignacco, and F. D. Rossini, J. Res. Natl. Bur. Stds., 35, 219 (1945).

interpolated logarithmically to 34.9°C. Interpolation of data by Smith (7) gives a value of 147.5 mm. and the interpolated value of Forzaiti *et al* (8) is 147.7 mm., both at 34.9°C. These determinations were made by the static method which would be expected to give somewhat higher values than the present work due to the difficulty in removing completely the foreign gas from the system used. The error of the method here employed is failure to condense completely the organic vapors. This would result in a value that would be low. The value for the vapor pressure of benzene obtained by this apparatus, when corrected by 0.3 mm. for the benzene not condensed, is 146.8 ± 0.4 mm. Thus the agreement with previously reported values is within one per cent.

Estimates are available for the vapor pressure of decalin at 35°C. From constants for Antoine's equation given by Camin and Rossini (9) the vapor pressure of pure *cis* and pure *trans* decalin can be calculated. Assuming that these compounds form an ideal solution, the vapor pressure of a mixture of 47 per cent *trans* decalin and 53 per cent *cis* decalin can be estimated to be 1.93 mm. The measurements were made by the static method, and extrapolation from approximately 100°C to 35°C was necessary. The value obtained by the present apparatus is 1.833 ± 0.021 mm.

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7. E. R. Smith, *ibid.*, *20*, 129 (1938).

8. A. F. Forzaiti, W. R. Norris, and F. D. Rossini, *ibid.*, *43*, 555 (1949).

9. D. L. Camin and F. D. Rossini, *J. Chem. Phys.*, *26*, 1173 (1955).

Neither of these values agree with those given in the previously reported data of Seyer and Mann (10). These authors reported data and a graph that do not agree with each other or with the values above. Also, neither the graph nor the data given shows a linear plot of log P vs. 1/T.

Completeness of Saturation of Nitrogen with Vapor.--To determine completeness of saturation of the nitrogen carrier by exposure to eight tubes containing liquid, a run was performed with only five tubes containing benzene. A value of 146.3 mm. was obtained for the vapor pressure of benzene. This is within experimental error of the average 146.5 ± 0.4 mm. obtained when eight tubes contained benzene.

In later experiments using a nitrobenzene solution in decalin, the concentration of several saturator compartments were determined by removing some of the solution after nine runs had been made. Although the first several compartments showed considerable concentration changes, the last three tubes had measured concentrations that were the same as that of the original solution within the experimental error. This showed that the latter compartments were unaffected, and saturation of the nitrogen must have been reached during passage through the first several tubes.

Completeness of Condensation of Organic Vapors.--Since benzene was the most volatile material being studied, it was used to determine whether or not all the organic vapors from the saturator were being condensed in the trap.

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10. W. F. Seyer and C. W. Mann, J. Am. Chem. Soc., 67, 328 (1945).

An experiment was run in the usual manner, except that the vapors which had already passed through the trap were passed through a sintered glass bubbler that was placed in pentane cooled to dry ice-acetone temperature. After 0.1981 cubic feet of nitrogen had passed through the system, the flow of nitrogen was stopped and the pentane solution was allowed to warm to room temperature. The concentration of benzene present was determined by its ultraviolet spectrum to be 0.2 g./l. This would indicate a loss of 0.008 g. of benzene during the run and would correspond to a vapor pressure of approximately 0.3 mm.

The vapor pressure of benzene at -77°C, the temperature of the trap, was estimated by Antoine's equation (11) to be 0.0058 mm. Thus it is seen that condensation of benzene was not quantitative, and the error introduced by ignoring the benzene lost is approximately 0.2 per cent.

Deviation from Atmospheric Pressure in the System.--Through the use of a "Y" tube, the line leading from the nitrogen source to the saturator (see Fig. 3) was connected to an air-exposed water-filled manometer. At a flow rate of 0.15 cubic feet of nitrogen per hour, the pressure head was 7.1 mm. of water or about 0.5 mm. of mercury. No visable change in the height of the pressure head was observed with nitrogen flow rates as high as 0.5 cubic feet per hour. It was concluded that passage of nitrogen caused no significant deviation from atmospheric pressure in the system.

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11. N. A. Lange, Handbook of Chemistry, 7th ed., Handbook Publishers, Inc., Sandusky, Ohio, 1949, p. 1434.

Maximum Amount of Condensate from Liquid Carry-over.-- Runs were made on a saturated solution of tri-p-tolyl phosphate to determine whether liquid droplets were being carried into the condensing trap as spray. This material was chosen as one that absorbed in the ultraviolet, but had a quite low vapor pressure. Standard solutions were used to determine its extinction coefficient. The saturated solution was found to be approximately 0.1 M.

A sufficient quantity of condensate was obtained to analyze without dilution, and its content of tri-p-tolyl phosphate was determined. The maximum content was estimated to be 1×10^{-5} M. Considering the original phosphate solution as 0.1 M, the maximum spray carry-over is estimated as 0.01 per cent, or no more than 2×10^{-6} ml. of spray was collected per liter of vapor. This was based on a typical run using approximately fourteen moles of vapor, about 0.04 moles of which are decalin.

Moisture in "Dried" Nitrogen.--It was found that the nitrogen used (cylinders from the Marks Oxygen Company) contained water vapor as an impurity. A variety of unsuccessful methods were used in attempts to remove this moisture. The most successful method was found to be that of passing the nitrogen through a trap immersed in dry ice and acetone, and then through a glass-wool-packed trap placed in liquid nitrogen. This still left moisture present to the extent of 0.00419 g. per cubic foot of nitrogen used. This value, an average of three determinations, was used as a correction factor for later runs. Were this correction not made, the results obtained would be high since water has a higher

vapor pressure than any substance studied except benzene. The condensate obtained by passing one cubic foot of nitrogen over decalin would weigh approximately 0.3700 g. If the 0.0042 g. of moisture were neglected, an error in weight of over one per cent would be introduced. This would result in a vapor pressure error of approximately 1.3 per cent if decalin was being collected.

CHAPTER III

PROCEDURE

Description of Materials Used.--The best grade of commercially available decalin (Eastman White Label, Eastman Organic Chemicals, Rochester, New York) was found to contain varying mixtures of cis and trans isomers as shown by vapor phase chromatography determinations. When all available decalin was mixed to prepare a quantity of uniform solvent, the mixture was shown to be approximately 48 per cent trans and 52 per cent cis. Although a vapor phase chromatogram showed only the two bands for the cis and trans isomers, and the ultraviolet spectrum showed no absorption that would indicate a definite impurity, the absorption of decalin condensates was not identical with the original decalin used. The first three grams of condensate showed greated absorption at wave lengths below 283 mμ. After the first three grams of decalin had been removed from the saturator, the difference in optical density between the condensate and the original decalin was no longer observed. A correction factor was obtained by dividing the difference in optical density at the particular wave length being studied by the dilution of the condensate with solvent decalin. This correction factor, never more than 0.006 optical density units, was applied to early runs to account for this difference in absorbance.

Later in the work, when additional solvent was required, an attempt was made to approach the original mixture of isomers. The

solvent mixture used with the bromobenzene was approximately 46 per cent trans and 54 per cent cis isomers. Although showing no observable impurity on vapor phase chromatography, the initial condensates from this mixture showed considerably more absorption than the decalin before being run through the apparatus. It was found that passing the solvent through a 75 cm. column packed with silica gel would remove most of the contaminant. A correction factor, never more than 0.006 optical density units, was used for the first 1.5 g. of condensate obtained in the runs thereafter. This factor was obtained in the same manner as in the case of the first solvent mixture.

The thiophene-free benzene used (Matheson, Coleman, and Bell) was distilled until analysis by vapor phase chromatography showed a single peak. The bromobenzene used (Eastman White Label) was distilled until a single peak was obtained by V. P. C. analysis. The m-dibromobenzene (Eastman White Label) showed no trace of impurities when subjected to V. P. C. analysis. The p-dibromobenzene (Eastman White Label) was recrystallized from methanol to a m.p. of 87-88°C.[1] The nitrobenzene was stock material, distilled until V. P. C. analysis showed a single peak. The p-dinitrobenzene (Matheson, Coleman, and Bell) was

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[1] The literature value for the m.p. of p-dibromobenzene is 87.3°C (12).

12. A. N. Campbell and L. A. Prodan, J. Am. Chem. Soc., 70, 553 (1948).

recrystallized from ethanol to a m.p. of 172-3°C.[2] The m-dinitrobenzene used had a m.p. of 88-9°C.[3]

Preparation of the Apparatus for a Determination.--The saturator pairs were cleaned by washing with detergent and then rinsed with water, ethanol, and acetone. They were dried by placing in an oven at 120°C for a period of not less than four hours.

During assembly and cooling of the saturator, nitrogen was passed through at a slow rate to prevent the collection of moisture. Each pair of saturators was removed separately from the oven and added to the assembly while hot. Each joint was lubricated thoroughly with Dow Corning silicone high vacuum grease. When the saturator was completely assembled, it was clamped in the rack and allowed to cool. Nitrogen was passed through the saturator during this time.

Into each of the first eight tubes there was placed ten milliliters of the liquid or solution whose vapor pressure was to be determined. In the case of solutions of benzene, however, it was found necessary to place solution in the first ten tubes. After filling, the saturator and rack were placed in the constant temperature bath and rocked for several hours to allow the contents to reach the temperature of the bath.

The traps used were washed with acetone and dried in the oven until needed.

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[2] The literature value for the m.p. of p-dinitrobenzene is 173.5°C. (13).

13. D. H. Andrews, G. Lynn, and J. Johnson, ibid., 48, 1274 (1926).

[3] The literature value for the m.p. of m-dinitrobenzene is 90.08°C. (13).

Nitrogen was obtained from cylinders of the Marks Oxygen Company. Most of the moisture was removed by passing the nitrogen throgh a trap cooled in dry ice and acetone and then through a trap that had been packed with glass-wool and immersed in liquid nitrogen.

Description of a Typical Determination.--A trap was removed from the oven and allowed to cool to room temperature while being swept with dried nitrogen, after which it was stoppered with small corks and weighed. It was swept with nitrogen while placed in a Dewar flask and cooled to the temperature of dry ice and acetone. After removing the nitrogen tube from the trap, the flask was quickly placed upon the rack and then connected to the exit tube from the saturator and to the tube leading to the wet test meter.

The dried nitrogen was introduced into the saturator through the inlet tube and allowed to pass over the liquid or solution while the saturator was rocked. The rate of nitrogen flow was measured and generally kept at 0.5 cubic feet per hour or less. The vapor-containing nitrogen passed through the saturator, out the heated exit tube, and into the cooled trap where the organic vapors were condensed. The nitrogen then passed into the wet test meter where its volume was measured.

The length of time of nitrogen flow was dependent upon the vapor pressure of the material being measured and the concentration of the solution being collected if a pure material was not being used. An average time was one to three hours, but times as long as six hours or as short as twenty minutes were encountered.

At the end of the determination, the trap was disconnected from

the system and one outlet tightly stoppered. The other outlet was loosely stoppered with a small cork until the trap and contents had warmed to room temperature whereupon the trap was again weighed. If a solution was collected, the solution was diluted with an amount of decalin sufficient to wash the sides of the trap, and then analyzed.

Analysis of Condensate.--The vapor pressure of the various organic materials was determined by multiplying the atmospheric pressure by the mole fraction of the particular material in the vapor from the saturator.

The number of moles of nitrogen was determined by measuring the volume of the nitrogen used, the temperature at which it was measured, and the pressure, corrected to dry conditions, under which the nitrogen was measured in the wet test meter. From this information, the term "n" in the ideal gas equation $PV = nRT$ can be calculated.

If a pure liquid was being studied, the weight gain of the trap during the run was obtained and corrected for the moisture present. This weight of organic compound, divided by the molecular weight of the compound gave the number of moles collected.

When a decalin solution was used, the weight of organic material was measured and its volume determined by dividing by the density of decalin. The assumption was made that the error introduced by weighing other materials as decalin is not great. In a typical run, decalin constituted over 99 per cent of the organic materials collected. The trap was then washed with a known amount of decalin to insure complete solution, and, if necessary, diluted further. The resulting solution was then analyzed by the use of a Beckmann DU Spectrophotometer.

It was found that all the materials studied absorb in the ultraviolet region at wave lengths where decalin does not absorb appreciably. Extinction coefficients were calculated at wave lengths of maximum absorbance for each of the materials used, and from these the concentration of the original condensate was calculated. Knowledge of the original volume and concentration was used to determine the number of moles condensed.

Calculation of Extinction Coefficients.--The extinction coefficients of the materials used as solutes were determined by analysis of known solutions. A Beckmann DU Spectrophotometer was used to measure the absorbance at wave lengths where the absorbance was at a maximum. The experimental data used to determine the extinction coefficients are shown in Tables 9 - 15 in the appendix. The extinction coefficients are given in Table 1 of the text. The wave lengths given are stated to the nearest millimicron.

The standard solutions used were made by weighing pure materials into a volumeric flask and diluting to the mark with decalin. These solutions were diluted quantitatively by weight to concentrations giving optical density readings between 0.2 and 0.6. The cell length used in all cases was one centimeter.

Table 1

Extinction Coefficients of Aromatic Compounds in Decalin

Compound	Wave Length, used, mμ	Slit Width, mm.	ε value
C_6H_6	261	0.28	$(1.429 \pm 0.034) \times 10^2$
C_6H_5Br	272	0.20	$(1.467 \pm 0.014) \times 10^2$
m-$C_6H_4Br_2$	279	0.20	$(3.130 \pm 0.039) \times 10^2$
p-$C_6H_4Br_2$	283	0.20	$(2.657 \pm 0.023) \times 10^2$
$C_6H_5NO_2$	254	0.28	$(8.490 \pm 0.081) \times 10^3$
m-$C_6H_4(NO_2)_2$	267	0.20	$(5.195 \pm 0.150) \times 10^3$
p-$C_6H_4(NO_2)_2$	255	0.15	$(1.105 \pm 0.017) \times 10^4$

CHAPTER IV

RESULTS

Vapor Pressure Measurements.--Tables 16 - 35 in the appendix give the data for the determination of the vapor pressures and partial pressures of the materials being investigated.

The following criteria were adopted for choosing the results necessary to obtain an average value for the vapor pressure of a material. Some standard was required, since the number of runs made before a constant value was reached was variable. In no case was the result from the passage of the first 0.4 cubic feet of nitrogen used. Runs were made until the last "n" runs, $n \geq 4$, had an average deviation of less than 3.5 per cent. The value of any one of these runs may be discarded if its deviation from the average of the other n-1 values is greater than four times the average deviation of the other values.

Two exceptions to this were made. In the case of 3×10^{-3} M nitrobenzene solution, experimentation in technique caused variation in answers, and two values out of eight were discarded. In the case of benzene solutions, rapid depletion would not allow the passage of 0.4 cubic feet of nitrogen to fill the saturator tubes not originally containing solution with organic vapor. In these cases, only 0.1 cubic feet of nitrogen was used before beginning measurement but two additional saturator tubes were loaded with solution to help establish equilibrium more quickly between the solution and the empty saturator

compartments.

Vapor Pressure of Pure Materials.--The vapor pressures of the liquid aromatic compounds were determined by measuring the pressure of the pure liquid. The vapor pressures of the solids studied were obtained by determining the partial pressure of the solid in a saturated solution in decalin. Since the undissolved solute is in equilibrium with the dissolved solute, and the dissolved solute in equilibrium with the vapor, it follows that the vapor must be in equilibrium with the undissolved solute. These values for vapor pressure are listed in Table 2. In Table 3, the vapor pressures for the decalin solutions are given.

Activity Coefficients.--The activity coefficient of solute X in solvent S is defined as the ratio of the activity of X to its molar concentration:

$$f_X^S = \frac{A_X}{M_X^S} .$$

If the solution is in equilibrium with the gas phase, then the activity of X in solution is numerically equal to the activity of X in the gas phase if both activities are expressed relative to the same standard state. If the gaseous state is taken as the standard state, and the gas is behaving ideally, the activity is equal to the partial pressure of the gas. Hence,

$$f_X^S = \frac{P_X}{M_X^S} .$$

Table 2

Vapor Pressures of Pure Materials at 35°C

Compound	Vapor Pressure, mm.
benzene	146.8 ± 0.4
bromobenzene	7.483 ± 0.083[a]
m-dibromobenzene	$(4.283 \pm 0.077) \times 10^{-1}$
p-dibromobenzene	$(1.335 \pm 0.045) \times 10^{-1}$[b]
nitrobenzene	$(6.000 \pm 0.089) \times 10^{-1}$[c]
m-dinitrobenzene	$(8.150 \pm 0.163) \times 10^{-4}$
p-dinitrobenzene	$2.246 \pm 0.047 \times 10^{-4}$
decalin	1.833 ± 0.021
toluene	46.7[d]
m-xylene	15.2[d]
p-xylene	15.8[d]

[a] Data of Dreyer et al. (14) give a value of 7.75 mm.

14. V. R. Dreyer, W. Martin, and U. Weber, J. pract. Chem., [4], 1, 324 (1955).

[b] Data of Walsh and Smith (15) give a value of 0.14 mm.

15. P. N. Walsh and N. O. Smith, J. Chem. Eng. Data, 6, 33 (1961).

[c] Data of Lynch and Wilke (16) give a value of 0.56 mm.

16. E. L. Lynch and C. R. Wilke, ibid., 5, 300 (1960).

[d] From data of Willingham et al. (6) probable precision of this data is ± 0.02 - 0.04 mm.

If the solutions are sufficiently dilute, f_X^S will be constant for varying values of M_X^S.

The partial pressure of materials under study were measured in quite dilute solutions or in a number of solutions of different concentrations in order to determine that the activity coefficient was constant. Where more than one pressure to concentration ratio was determined, the values obtained were averaged. For other substances, a single measurement was made.

The experimental data for all determinations are found in Tables 9 - 38 in the appendix. Tables 36 - 38 give the data for the individual determinations of the solubility in decalin at 35°C of the solid compounds studied.

From the results of Table 3 for solutions in decalin, the activity coefficients were calculated. These results are given in Table 4.

The activity coefficients for solutions in water were obtained in a somewhat different fashion. In such cases, considering a saturated solution only, the expression

$$f_X^{water} = \frac{P_X}{sol_X^{water}}$$

is obtained, where the term sol_X^{water} is the concentration in moles per liter of a saturated solution of substance X in water. Assuming that the solute in equilibrium with the saturated solution contains so little water that its activity is the same as that of the pure substance, P_X may be taken as the vapor pressure of the pure substance. The solubilities of these materials in water are available from previous

Table 3

Partial Pressures of Solutions in Decalin

Compound	Conc., M	Partial Pressure, mm.
benzene	approx. 10^{-1}	[a]
	3.682×10^{-2}	1.180 ± 0.004
	1.072×10^{-2}	$(3.383 \pm 0.049) \times 10^{-1}$
bromobenzene	1.045×10^{-2}	$(1.927 \pm 0.031) \times 10^{-2}$
	9.769×10^{-2}	$(1.804 \pm 0.040) \times 10^{-1}$
m-dibromobenzene	9.937×10^{-2}	$(1.236 \pm 0.013) \times 10^{-2}$
	1.014×10^{-2}	$(1.300 \pm 0.019) \times 10^{-3}$
p-dibromobenzene	$(9.790 \pm 0.340) \times 10^{-1}$ [b]	$(1.335 \pm 0.045) \times 10^{-1}$
	1.061×10^{-2}	$(1.386 \pm 0.043) \times 10^{-3}$
	3.211×10^{-2}	$(4.224 \pm 0.134) \times 10^{-3}$
nitrobenzene	3.462×10^{-3}	$(2.983 \pm 0.049) \times 10^{-3}$
	3.409×10^{-4}	$(2.845 \pm 0.075) \times 10^{-4}$
	1.150×10^{-3}	$(9.003 \pm 0.090) \times 10^{-4}$
m-dinitrobenzene	$(2.579 \pm 0.051) \times 10^{-2}$ [b]	$(8.150 \pm 0.163) \times 10^{-4}$
p-dinitrobenzene	$(5.600 \pm 0.261) \times 10^{-3}$ [b]	$(2.246 \pm 0.047) \times 10^{-4}$

[a] Two different concentrations of approximately 0.1 M were used.

[b] These are saturated solutions.

experimental work and are listed in Table 5.

Calculation of Tau Differences.--The difference between tau in phase A, τ^A, and tau in phase B, τ^B, is given by the following formula. (See introduction for definition of terms.)

$$\log \frac{f^B_{PhH}\, f^B_{p\text{-}PhX_2}}{(f^B_{PhX})^2} = (\tau^A_p - \tau^B_p)(\sigma_{p\text{-}X})^2$$

The activity coefficients are those in phase B with respect to A as a standard state. A similar equation can be written for the meta case.

Tau differences can be calculated between tau in the gas phase, τ^G, and tau in solutions in decalin, τ^D, by the equation

$$\log \frac{f_{PhH}\, f_{p\text{-}PhX_2}}{(f_{PhX})^2} = (\tau^G_p - \tau^D_p)(\sigma_{p\text{-}X})^2 ,$$

where $f_x = \frac{P_x}{\text{conc.}}$

Tau differences between the gas phase and water are calculated from the following equation.

$$\log \frac{P_{PhH}\, P_{p\text{-}PhX_2}}{(P_{PhX})^2} \frac{(sol^W_{PhX})^2}{sol^W_{PhH}\, sol^W_{p\text{-}PhX_2}} = (\tau^G_p - \tau^W_p)(\sigma_{p\text{-}X})^2$$

These tau differences are summarized in Tables 6 and 7.

Table 4

Activity Coefficients of Compounds in Decalin Solutions of Known Concentration with Reference to the Gas Phase.

Compound	Press./Conc.
benzene	31.58 ± 0.31
bromobenzene	1.846 ± 0.002
m-dibromobenzene	0.1262 ± 0.0020
p-dibromobenzene	0.1328 ± 0.0024
nitrobenzene	0.8263 ± 0.0290
m-dinitrobenzene	$(3.160 \pm 0.089) \times 10^{-2}$
p-dinitrobenzene	$(4.011 \pm 0.202) \times 10^{-2}$

Table 5

Solubilities of Certain Organic Compounds in Water at 35°C[a]

Compound	Solubility, M
benzene	2.420×10^{-2}[b]
bromobenzene	$(2.922 \pm 0.048) \times 10^{-3}$
m-dibromobenzene	$(2.860 \pm 0.123) \times 10^{-4}$
p-dibromobenzene	$(1.120 \pm 0.051) \times 10^{-4}$
nitrobenzene	$(1.835 \pm 0.021) \times 10^{-2}$
m-dinitrobenzene	$(4.672 \pm 0.068) \times 10^{-3}$
p-dinitrobenzene	$(6.167 \pm 0.143) \times 10^{-4}$
toluene	7.13×10^{-3}[b]
m-xylene	1.92×10^{-3}[b]
pxylene	1.94×10^{-3}[b]

[a] Unless otherwise stated, these data were obtained by Ramsey (17).

17. O. B. Ramsey, unpublished results.

[b] Data of Bohon and Claussen (18). Precision is approximately three per cent.

18. R. L. Bohon and W. F. Claussen, J. Am. Chem. Soc., 73, 1571 (1951).

Treatment of Average Deviations.--Statistical methods are available for the combination of the standard deviations of complex functions (19). If the function, F, is equal to AB, then

$$\Delta_F = (\Delta_A{}^2 B^2 + \Delta_B{}^2 A^2)^{1/2}$$

If the function, F, is equal to A/B, then

$$\Delta_F = \frac{A}{B}\left(\frac{\Delta_A{}^2}{A^2} + \frac{\Delta_B{}^2}{B^2}\right)^{1/2}$$

If the function, F, is equal to C^2, then

$$\Delta_F = 2\Delta_C C$$

If the function, F, is equal to AB/C^2, then

$$\Delta_F = \frac{AB}{C^2}\left(\frac{\Delta_A{}^2}{A^2} + \frac{\Delta_B{}^2}{B^2} + \frac{4\Delta_C{}^2}{C^2}\right)^{1/2}$$

If the function, F, is equal to C^2/AB, then

$$\Delta_F = \frac{C^2}{AB}\left(\frac{\Delta_A{}^2}{A^2} + \frac{\Delta_B{}^2}{B^2} + \frac{4\Delta_C{}^2}{C^2}\right)^{1/2}$$

The term Δ refers to the root mean square deviation and is also termed the standard deviation. This is related to the average deviation,

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19. G. B. Cook and J. F. Duncan, Modern Radiochemical Practice, The Clarendon Press, Oxford, England, 1952, p. 60.

a, by the expression $a = \Delta\left(\frac{2}{\pi}\right)^{1/2}$ (20).

In the calculations that follow, the experimental average deviations were converted to standard deviations and statistically combined according to the above formulas. The combined standard deviation was then related back to an average deviation and the deviation of tau differences then calculated.

Correlation of Tau Differences.--If a plot is made of the logarithm of the mathematically combined activity coefficients vs. the σ^2 term in the equation.

$$\log \frac{f^B_{PhX}\, f^B_{p\text{-}PhX_2}}{(f^B_{PhX})^2} = (\tau_A - \tau'_B)(\sigma_{p\text{-}x})^2, \text{ a straight line}$$

should result whose slope is the difference in tau values, $\Delta\tau$. These plots are shown in Figs. 4 and 5.

Data for toluene and meta and para xylene, shown in Fig. 5, were obtained from reported literature values for solubility in water (18) and the vapor pressures of the pure materials (6,16).

Application of Results.--The idea of molecular properties being additive was proposed by Benson and Buss (21) for disproportion reactions of the type RNR + SNS $\leftrightharpoons$ 2RNS. For any molecular property, the difference in that property should approach zero as the separation between R and S

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20. H. Margenau and G. M. Murphy, The Mathematics of Chemistry and Physics, D. Van Nostrand and Company, Inc., New York, N. Y., 1943, p. 496.

21. S. W. Benson and J. H. Buss, J. Chem. Phys., 29, 546 (1958).

Table 6

Summary of Tau Differences from Activity Coefficients in Water with Reference to the Vapor State.

Substituent	$\frac{f_{PhH}\ f_{PhX_2}}{(f_{PhX})^2}$	σ value[a]	$\Delta\tau_p$	$\Delta\tau_m$
m-Br	1.379 ± 0.098	0.391	----	0.90 ± 0.20
p-Br	1.099 ± 0.075	0.232	0.63 ± 0.48	----
m-NO_2	0.988 ± 0.047	0.710	----	0.01 ± 0.04
p-NO_2	2.062 ± 0.096	0.778	0.52 ± 0.03	----
m-CH_3	1.11 ± 0.10	-0.069	----	11.6 ±11.4
p-CH_3	1.16 ± 0.13	-0.170	3.65 ± 2.90	----

[a] The σ values are those reported by Hine. (22).

22. J. Hine, Physical Organic Chemistry, McGraw-Hill Book Book Company, Inc., New York, N. Y., 1956, p. 72.

Table 7

Summary of Tau Differences from Activity Coefficients in Decalin Solution with Reference to the Vapor State

Substituent	$\frac{f_{PhH}\, f_{PhX_2}}{(f_{PhX})^2}$	σ value[a]	$\Delta\tau_p$	$\Delta\tau_m$
m-Br	1.172 ± 0.054	0.391	----	0.45 ± 0.13
p-Br	1.233 ± 0.047	0.232	1.40 ± 0.25	----
m-NO_2	1.461 ± 0.112	0.710	----	0.33 ± 0.07
p-NO_2	1.861 ± 0.162	0.778	0.44 ± 0.06	----

[a] The σ values are those reported by Hine (22).

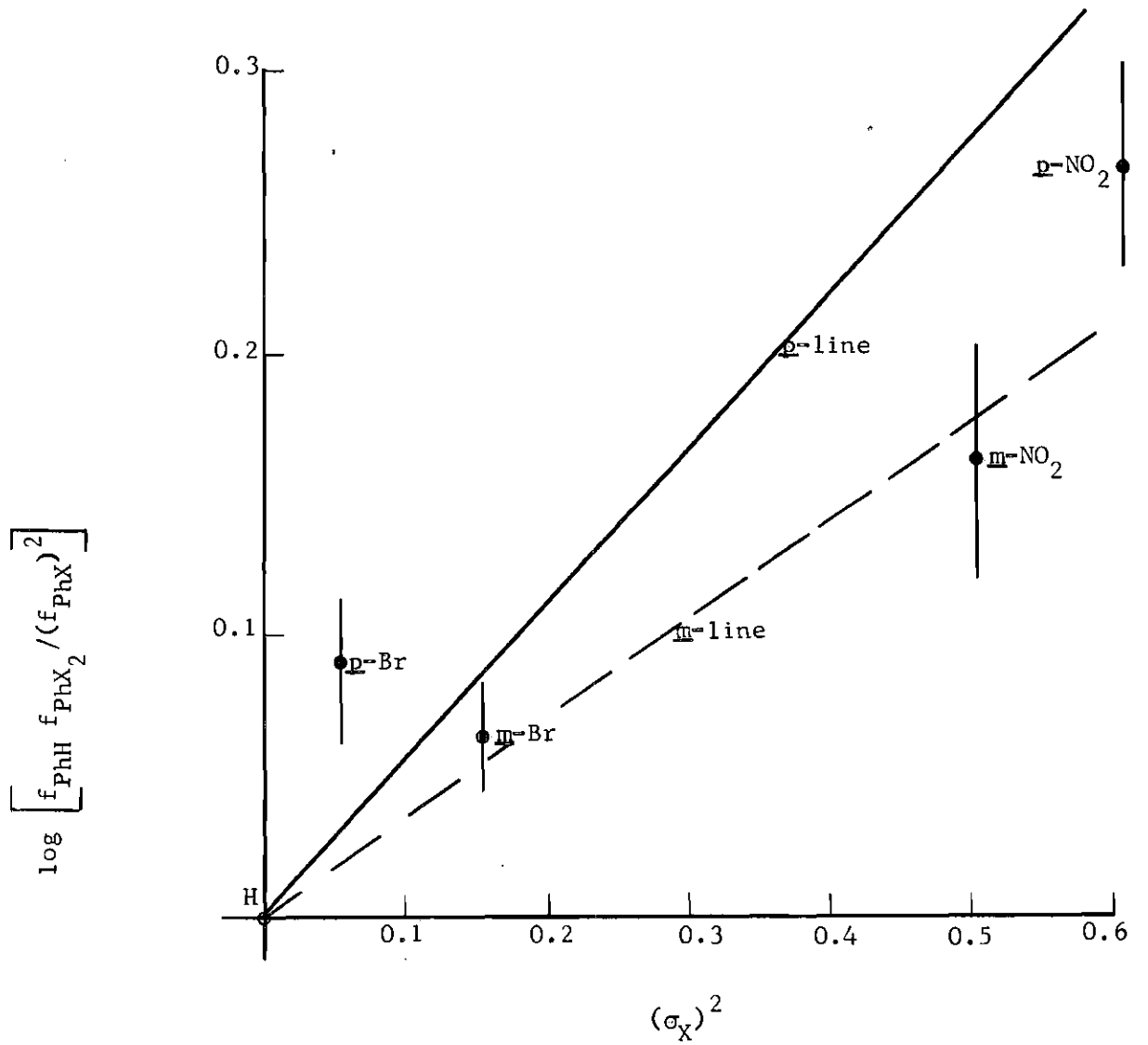

Fig. 4. Plot of Log $\left[f_{PhH}\, f_{PhX_2}/(f_{PhX})^2\right]$ vs. σ_X^2 - Activity Coefficients in Decalin with Reference to the Vapor State.

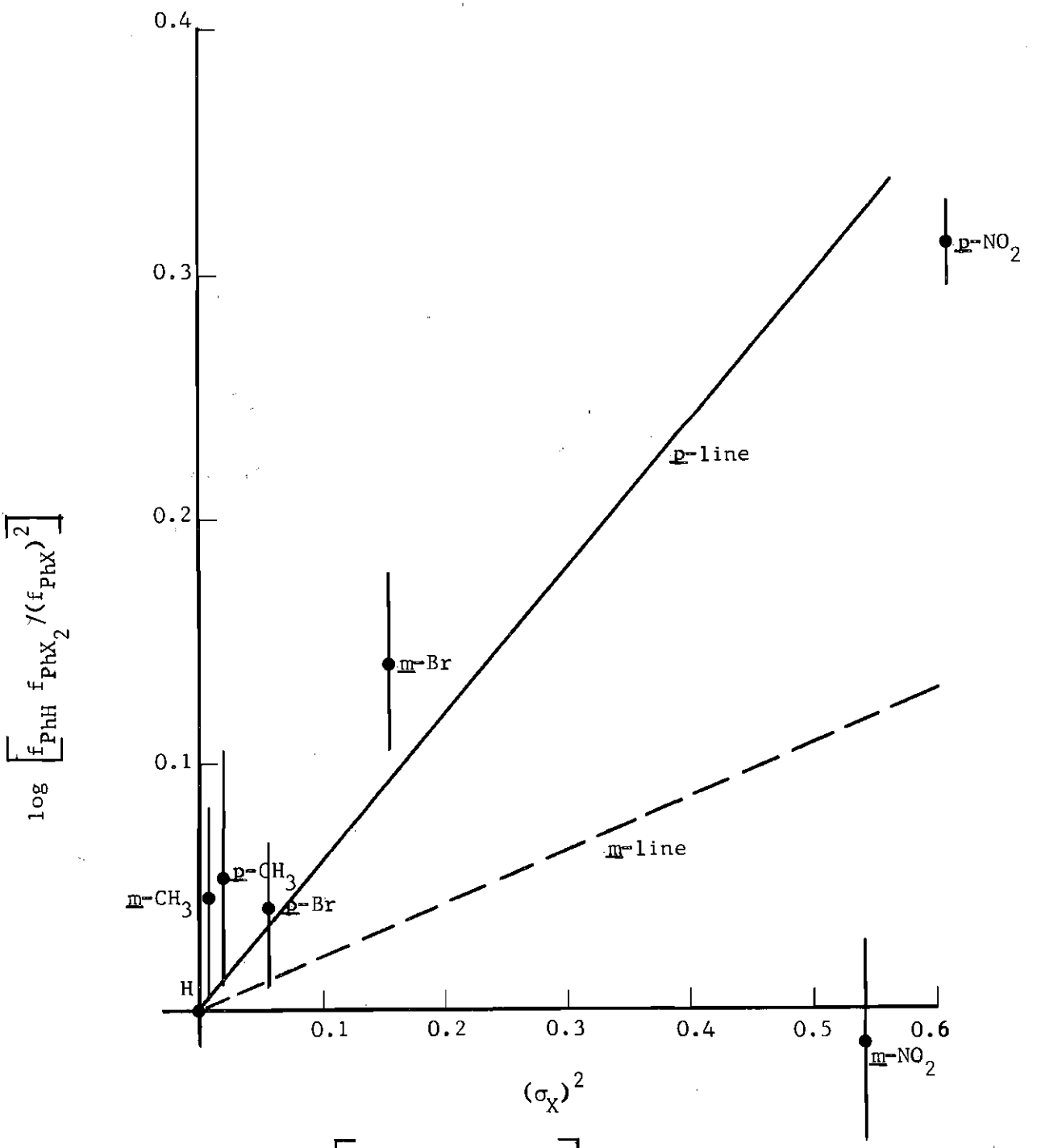

Fig. 5. Plot of Log $\left[f_{PhH}\ f_{PhX_2}/(f_{PhX})^2\right]$ vs. σ_X^2 - Activity Coefficients in Water with References to the Vapor State.

groups in the molecule increases. In a limiting case where the distance between groups becomes so large that they no longer influence one another, the atoms should contribute additively to many molecular properties. The additivity accuracy should increase with large molecules.

The equation proposed by Hine is an extension of this idea. It considers the effects between the two groups when the distance between them is not infinitely large. In the expression

$$\log \frac{f_{PhH}\, f_{PhX_2}}{(f_{PhX})^2} = \Delta\tau(\sigma_X)^2$$

if the proposal of Benson and Buss may be applied to activity coefficients, the combined activity coefficient should approach unity as the distance between X groups becomes infinite. This would cause the logarithm to become zero and tau would become zero as well. This is in accord with tau representing the transmittance of effect between the two groups which would be non-existent at infinite distance between groups. One would also predict that if tau were other than zero, it would be a positive number representing a positive transmittal of effect between two groups not sufficiently far apart to be independent of each other.

Measurements have been made in two very different liquid media, water and a saturated hydrocarbon decalin. In addition, these measurements give information about a third medium, the gas phase.

According to the above equation, a plot of the logarithm of the activity coefficient term vs. σ^2, as shown in Fig. 4 and Fig. 5, should give a straight line whose slope is the difference in tau values for

the two media under consideration. For the data of Fig. 4, the activity coefficients in decalin, both *meta* and *para* substituents give points that lie fairly near a straight line. The plot of the data for activity coefficients in water (Fig. 5) shows that the points for the *para* substituents lie near a straight line but those for the *meta* substituents[1] do not. The slope of the lines in Figs. 4 and 5 show τ_p differences of 0.53 and 0.60 and τ_m differences of 0.35 and 0.22[1] between decalin and the gas phase and between water and the gas phase, respectively. These differences are in the direction expected. However, the differences in *tau* are no larger than the uncertainty that already exists concerning the value of *tau* in aqueous solution, where τ_m values of 2.66, 2.84, 3.53, and 3.57 and τ_p values of 2.87, 2.91, 3.05, and 3.50 have been calculated (2,3). In addition, a combination of the *tau* differences between water and the vapor state, and between decalin and the vapor state, gives a τ_p difference of 0.07 and a τ_m difference of -0.13 between water and decalin. Thus values not significantly different from zero are observed between *tau* for water, whose dielectric constant is 80, and *tau* for decalin, whose dielectric constant is 2.2. Just as previous work had given τ_m and τ_p values within experimental error of each other (2,3), the $\Delta\tau_m$'s and $\Delta\tau_p$'s are within experimental error of each other.

The average deviation of the points in Figs. 4 and 5 (excluding the points for hydrogen which fit by definition) is 0.052 log units.

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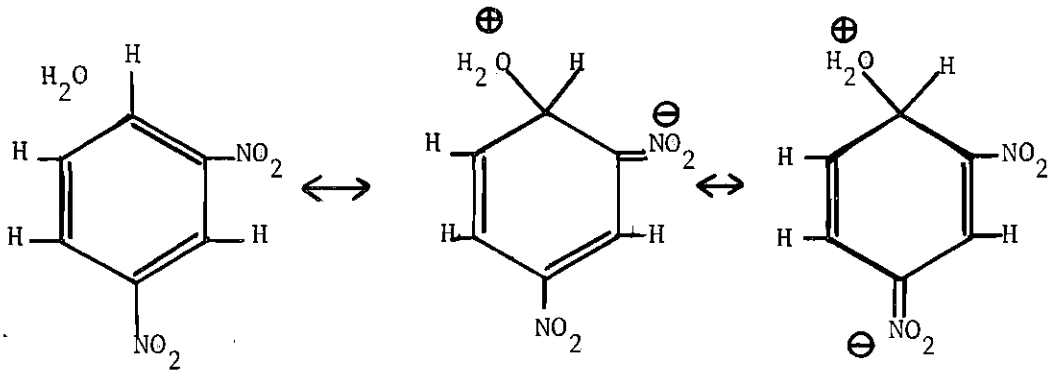
[1] This is the best line that can be drawn for these points, but the deviations are so large that the equation is not really obeyed.

This value is smaller than the 0.071 log units found by Hammett for the first 52 reaction series to which the Hammett equation was applied (23). Nevertheless, it seems probable that there are specific solvent aromatic interactions that result in deviations. The deviation of the point for m-nitro in Fig. 5 may be due to such an interaction. Since the only datum used in determining this point that was not used in determining the m-nitro point in Fig. 4, where reasonable agreement exists, is the solubility of m-dinitrobenzene in water, there may be an interaction between the basic oxygen of water and the carbon atoms ortho and para to the nitro groups in m-dinitrobenzene.



Such an interaction is analogous to that which results in the purple solution of m-dinitrobenzene in liquid ammonia (24). Although the

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23. L. P. Hammett, Physical Organic Chemistry, McGraw-Hill Book Company, Inc., New York, N. Y., 1940, p. 192.

24. J. D. Farr, C. C. Bard, and G. W. Wheland, J. Am. Chem. Soc., 71, 2013 (1949).

contribution of the second and third resonance forms may not be large enough to change the electronic structure of m-dinitrobenzene greatly, it may account for the increased solubility in water which causes the activity coefficient for this compound in water with reference to the gas phase to be smaller than expected.

It is also possible that the solid in equilibrium with a saturated aqueous solution may be hydrated or that in equilibrium with a saturated decalin solution may contain decalin of crystallization. Therefore, the assumption that the solid phase present in the two cases is the same is not warranted. Were this point omitted, the average deviation of points in Figs. 4 and 5 would be 0.036.

These data give several important indications. To whatever extent the transmission of substituent effect in a benzene ring has been measured in terms of the proportionality constants τ_m and τ_p, the values of these constants change very little with the nature of the solvent. It is also seen that the equilibrium constants for disproportionation of toluene, bromobenzene, and nitrobenzene:

$$2C_6H_5X \rightleftharpoons C_6H_6 + C_6H_4X_2$$

will change by activity coefficient ratios listed in Tables 6 and 7. Over the range of media studied, water, decalin, and gas, no change will be more than about two fold.

These results may apply generally to interactions of electrically neutral substituents which are the only type studied here. It is not reasonable to expect that σ constants for electrically charged species would be solvent-independent.

It has been shown (2) for the reaction

$$ArX_1 \rightleftharpoons ArX_2,$$

that $$\rho = \tau(\sigma_{X_1} - \sigma_{X_2})$$

If tau is relatively solvent-independent as is shown above then observed changes in ρ must be due to changes in σ_{X_1} or σ_{X_2}. In almost all of the cases where ρ does change, either X_1 or X_2 is a charged group, and changes in σ might be expected due to substituent-solvent interaction.

CHAPTER V

CONCLUSION

The data obtained in the present work support the concept that in a disproportion reaction of the type $PhX_2 + PhH \rightleftarrows 2PhX$, the molecular properties of the mono-substituted product can be expressed as a combination of those of the non-substituted and disubstituted reactants. The ratio $f_{PhH}\, f_{PhX_2}/(f_{PhX})^2$ is reasonably close to unity. The deviations from unity show that placing groups in <u>meta</u> or <u>para</u> positions on a benzene ring does not separate them sufficiently to make them independent of one another. A previously derived equation correlates these differences with reasonable accuracy.

APPENDIX

Corrections on Data Presented

All of the values for weights of condensates in the following tables are uncorrected for the weight of water collected. To determine the weight of moisture in any example, multiply the cubic feet of nitrogen by 0.00419 g. H_2O/cu. ft. To determine the weight of the moisture-free decalin solution, subtract the appropriate weight of moisture from the weight of condensate.

Some of the optical densities, (O.D.), given in the following tables have been corrected for differences in absorption between decalin that has come from the saturator and the original decalin used. These values that have been corrected are indicated by a "c" after the optical density value. To find the correction applied, take the optical density difference at the appropriate wave length from Table 8 and divide by the extent to which the solution was diluted. Addition of this factor to the optical density value given will provide the optical density of the uncorrected dilute condensate.

In general, dilutions were made on a weight basis. In some cases where the dilution is indicated as being on a volume basis, original weights were converted to the volume given and then diluted in a volumetric flask.

Table 8

Differences in Absorption Between Decalin Condensed from the Saturator and the Original Decalin at Various Wave Lengths.

Wave Length, (mμ)	Optical Density difference
254	0.068
255	0.068
261	0.025
267	0.020
272	0.030
279	0.046
283	0.061

Sample Calculation of the Partial Pressure of Bromobenzene in a 1.045 x 10^{-2} M Solution in Decalin.

In the first run made on this solution, 0.6999 cu. ft. of nitrogen was used at an average temperature of 76.3°F and a barometric pressure of 736.9 mm., and 0.2343 g. of condensate was collected. This was diluted with decalin to 6.606 g. and analyzed on a Beckman DU Spectrophotometer. It was found to have an optical density of 0.384.

Correction for moisture collected:

g. of condensate	0.2343 g.
g. of moisture = 0.6999 cu. ft. x 0.00419 g./ H_2O cu ft.	0.0029
	0.2314 g.

Concentration of dilute solution: ϵ for C_6H_5Br = 0.1467×10^3

cell length = 1 cm.

$$C = \frac{O.D.}{\epsilon \times l}$$

$$C = \frac{0.384}{0.1467 \times 10^3} = 2.618 \times 10^{-3}$$

Concentration of original solution

$$M_1 G_1 = M_2 G_2$$

$$(2.618 \times 10^{-3})(6.606) = M_2 (0.2343)$$

$$M = 7.379 \times 10^{-2}$$

Volume of original solution: (as decalin)

$$V = \frac{wt.}{D.} = \frac{0.2314}{0.884} = 0.2618 \text{ ml.}$$

No. of moles C_6H_5Br collected:

$$\text{no. of moles} = M.\ V_{\text{liters}}$$

$$= (7.379 \times 10^{-2} \text{ moles/l.}) \times 0.2618 \times 10^{-3} \text{ l.}$$

$$= 1.932 \times 10^{-5} \text{ moles}$$

No. of moles of N_2:

$$n = \frac{PV}{RT}$$

73.6°F = 24.6°C = 297.8°A

736.9 mm. = bar. press.

23.2 mm. = vapor press. water at 24.6°C.

713.7 = press. of N_2 if dry

$$n = \frac{(713.7/760) \text{ atm.} \times 0.6999 \text{ cu. ft.} \times (28.32 \text{ l./cu. ft.})}{(0.08206 \text{ atm. l. /mole °A}) \times 297.8°A)}$$

$$n_{N_2} = 0.7613$$

No. of moles of decalin:

$$n_{dec} = \frac{\text{g. decalin}}{\text{g. mol. wt.}} = \frac{0.2314}{1.382} = 0.001674$$

No. of moles (total):

$$\text{moles (total)} = \text{moles } N_2 + \text{moles dec.} + \text{moles } C_6H_5Br$$

$$= 0.7613 + 0.0017 + 0.00001932$$

$$= 0.7630$$

Partial Pressure C_6H_5Br:

$$P_{C_6H_5Br} = \frac{\text{moles } C_6H_5Br \times \text{bar. press.}}{\text{moles (total}}$$

$$P_{C_6H_5Br} = \frac{1.932 \times 10^{-5} \times 736.9 \text{ mm.}}{0.7630} = 1.866 \times 10^{-2} \text{ mm.}$$

Table 9

Extinction Coefficient of Benzene in Decalin at a Wave Length of 261 mμ and Slit Width of 0.28 mm.

g. diluted to 10 ml.	Dilution, ml. to ml.	Further Dilution, g. to g.	O. D.	ε
0.1289	0.4173 - 10.00	a) 1.293 - 3.540	0.371	147.5
		b) 1.778 - 3.663	0.485	145.1
0.1113	a)0.1139 - 10.00		0.226	139.2
	b)0.1486 - 10.00		0.296	139.8

Av. ε = 142.9 ± 3.4

Table 10

Extinction Coefficient of Bromobenzene in Decalin at a Wave Length of 272 mμ and Slit Width of 0.20 mm.

g. diluted to 10 ml.	Dilution, g. to g.	Further Dilution, g. to g.	O. D.	ε
0.2829	0.3189 - 8.883	a)0.9331 - 3.478	0.258	148.6
		b)1.338 - 3.429	0.367	145.3
0.2131	0.3349 - 8.944	a)2.151 - 3.791	0.420	145.3
		b)1.939 - 3.557	0.409	147.7

Av. $\varepsilon = 146.7 \pm 1.4$

Table 11

Extinction Coefficient of m-Dibromobenzene in Decalin at a Wave Length of 279 mμ and Slit Width of 0.20 mm.

g. Diluted to 10 ml.	Dilution, g. to g.		Further Dilution, g. to g.	O. D.	ε
0.3188	0.2292	8.843	a) 1.464 - 3.771	0.419	308.3
			b) 0.9910 - 3.729	0.300	319.8
0.2475	0.1131	3.741	a) 1.483 - 3.700	0.394	310.0
			b) 1.110 - 3.625	0.305	314.2

Av. ϵ = 313.0 ± 3.9

Table 12

Extinction Coefficient of p-Dibromobenzene in Decalin at a Wave Length of 283 mμ and Slit Width of 0.20 mm.

g. Diluted to 10 ml.	O. D.	ε
3.949×10^{-3}	0.439	262.2
4.578×10^{-3}	0.521	268.4
5.119×10^{-3}	0.578	266.4

Av. ε = 265.7 ± 2.3

Table 13

Extinction Coefficient of Nitrobenzene in Decalin at 254 mμ and Slit Width of 0.28 mm.

g. $C_6H_5NO_2$ diluted to 10 ml.	Dilution, g. to g.	Further Dilution, g. to g.	O. D.	ε
4.262×10^{-2}	1.2501 - 9.2111			
	0.9854*- 8.6401	a) none	0.449	8,380
		b) 1.6535-3.3878	0.225	8,604
		c) 2.2481-3.7375	0.271	8,408
9.708×10^{-3}	0.0642 - 8.7939	a) none	0.494	8,581
		b) 1.8392-3.6053	0.249	8,478

Av. ε = 8,490 ± 81

* This solution was made from that dilution given directly above.

Table 14

Extinction Coefficient of m-Dinitrobenzene in Decalin at a Wave Length of 267 mμ and Slit Width of 0.20 mm.

Conc. of Solution, M	O. D.	ε
1.19×10^{-4}	0.589	4,950
9.49×10^{-5}	0.493	5,190
7.31×10^{-5}	0.402	5,500
5.58×10^{-5}	0.289	5,140

Av. $\varepsilon = 5{,}195 \pm 150$

Table 15

Extinction Coefficient of p-Dinitrobenzene in Decalin at a Wave Length of 255 mμ and Slit Width of 0.15 mm.

Dilution,[a] g. to g.	O. D.	ε
0.5409 - 3.6201	0.470	11,320
0.5954 - 3.6628	0.488	10,810
0.4194 - 3.5429	0.366	11,110
0.6619 - 3.6473	0.552	10,950

Av. ϵ = 11,050 $\pm$ 170

[a] 4.262×10^{-2} G. of p-dinitrobenzene was diluted to 10.0 ml. in a volumetric flask. The dilutions given are from this solution.

Table 16

Vapor Pressure of Benzene

Cu. ft. N_2	Temp., °F	Bar. Press., mm.	g. Cond.	P., mm.
0.1773	77.2	744.2	3.7665	147.3
0.1897	83.0	744.0	3.9603	146.3
0.1981	82.9	740.9	4.0845	146.4
0.1999	80.3	740.2	4.1829	146.9
0.2008	85.3	740.2	4.0909	145.9

Av. P. = 146.5 $\pm$ 0.4 mm.

Special Case of Benzene Solutions

It was found that solutions of benzene in decalin were depleted in benzene solute so rapidly that special precatutions were necessary. An additional two saturator tubes were loaded with solution to decrease the time required to equilibrate the empty tubes with organic vapors. Since minimum quantities of nitrogen were used, the amounts of condensate that resulted were too small to weigh accurately. Decalin was added in known amounts while the condensate was still frozen. This served to wash the trap and retard loss of benzene through evaporation. The weight of benzene solution originally collected was neglected. The resulting solution was suitably diluted and analyzed.

Even so, depletion of all compartments was a factor requiring correction. Analyses of solutions remaining in the saturator after the passage of 0.4 cubic foot of nitrogen showed 5.32 per cent depletion in the last compartment that contained solution. Assuming a linear depletion, this would correspond to a 1.33 per cent depletion per run of 0.1 cubic foot. Thus, a correction factor of one-half this depletion would be applied to the first run, one and one-half this percentage to the second run, two and one-half to the third run, and three and one-half to the fourth run. These factors were used for the corrected concentration shown in the tables dealing with benzene solutions. These tables are 17, 18, and 19.

Table 17

Partial Pressures of Benzene in Approximately 0.1 M Solutions in Decalin

Conc., M	Corr. Conc., M	Cu. ft. N_2	Temp., °F	Bar. Press., mm.	g. Cond. + decalin	Dilution, g. to g.	O. D.	P., mm.	P./Conc.
0.1123	0.1146[a]	0.1000	76.3	748.0	4.378	0.0909 - 3.616	0.362	3.364	30.57
0.1118	0.1141[a]	0.1003	72.5	741.9	4.565	0.0873 - 3.727	0.337	3.457	31.56
0.1118	0.1156[b]	0.1000	71.8	741.9	5.491	0.1709 - 3.751	0.529	3.360	31.09
0.1118	0.1173[c]	0.1000	71.7	741.9	4.535	0.1208 - 3.610	0.468	3.340	31.27

Av. P./Conc. = 31.12 ± 0.31

[a] These runs correspond to the second 0.1 cu. ft. of N_2 passed through the saturator.

[b] This run corresponds to the third 0.1 cu. ft. of N_2 used.

[c] This run corresponds to the fourth 0.1 cu. ft. of N_2 used.

Table 18

Partial Pressure of Benzene in a 1.072×10^{-2} M Solution in Decalin

Cu. ft. N_2	Temp., °F	Bar. Press., mm.	g. Cond. + decalin	Dilution, g. to g.	O. D.	Press., mm.	Corr. Conc., M	P./Conc.
0.1000[a]	76.6	740.0	4.364	0.8406 - 3.581	0.329	0.3280	1.094×10^{-2}	31.22
0.1000[b]	77.0	740.0	4.528	0.9682 - 3.689	0.349	0.3233	1.109×10^{-2}	31.19
0.1001[c]	77.5	740.0	4.479	0.9417 - 3.581	0.360	0.3295	1.124×10^{-2}	32.24

Av. P./Conc. = 31.55 ± 0.46

[a] This run corresponds to the second 0.1 cu. ft. of N_2 used.

[b] This run corresponds to the third 0.1 cu. ft. of N_2 used.

[c] This run corresponds to the fourth 0.1 cu. ft. of N_2 used.

Table 19

Partial Pressure of Benzene in a 3.682×10^{-2} M Solution in Decalin

Cu. ft. N_2	Temp., °F	Bar. Press., mm.	g. Cond. + decalin	Dilution, g. to g.	O. D.	Press., mm.	Corr. Conc., M	P./Conc.
0.1000[a]	74.5	744.8	4.4311	0.2308 - 3.486	0.325	1.158	3.757×10^{-2}	32.09
0.1000[b]	75.2	744.8	4.4049	0.2096 - 3.583	0.285	1.144	3.809×10^{-2}	32.14
0.1001[c]	75.6	744.8	4.2289	0.2844 - 3.541	0.398	1.119	3.862×10^{-2}	31.88

Av. P./Conc. = 32.04 ± 0.10

[a] This run corresponds to the second 0.1 cu. ft. of N_2 used.

[b] This run corresponds to the third 0.1 cu. ft. of N_2 used.

[c] This run corresponds to the fourth 0.1 cu. ft. of N_2 used.

Table 20

Vapor Pressure of Bromobenzene

Cu. ft. N_2	Temp., °F	Bar. Press., mm.	g. Cond.	P., mm.
0.2001	75.6	744.9	0.3481	7.393
0.2000	75.0	744.9	0.3508	7.444
0.2000	75.0	744.9	0.3604	7.647
0.2002	79.0	743.0	0.3472	7.443

Av. P. = 7.483 $\pm$ 0.083 mm.

Table 21

Partial Pressure of Bromobenzene in a 9.769×10^{-2} M Solution in Decalin

Cu. ft., N_2	Temp., °F	Bar. Press., mm.	Dilution, g. to g.	O. D.	P., mm.
0.4000	71.2	733.3	0.1512[a] - 8.140 0.9286 - 3.656	0.431	0.1753
0.4000	71.0	733.3	0.1545[a] - 8.175 0.5885 - 3.724	0.274	0.1799
0.8000	70.9	733.3	0.3310[a] - 8.293 0.5133 - 3.762	0.461	0.1778
0.5000	70.3	733.3	0.2087[a] - 8.449 0.6093 - 3.765	0.356	0.1886

Av. P. = 0.1804 ± 0.0041 mm.

[a] Grams of condensate

Table 22

Partial Pressure of Bromobenzene in 1.045×10^{-2} M Solution in Decalin

Cu. ft. N_2	Temp., °F	Bar. Press., mm.	Dilution, g. to g.	O. D.	10^2P., mm.
0.6999	76.3	736.9	0.2343[a] - 6.606	0.384c	1.866
0.4000	77.4	736.9	0.1521[a] - 4.581	0.334c	1.975
0.4002	69.2	736.0	0.1541[a] - 4.156	0.367c	1.926
0.4001	70.5	736.0	0.1669[a] - 3.948	0.388c	1.941

Av. P. = $(1.927 \pm 0.031) \times 10^{-2}$ mm.

[a] Grams of condensate

Table 23

Vapor Pressure of m-Dibromobenzene

Cu. ft. of N_2	Temp., °F	Bar. Press., mm.	g. Cond.	P., mm.
0.6003	72.4	742.2	0.0916	0.4212
0.7002	73.5	742.2	0.1101	0.4357
0.7000	74.5	742.2	0.1059	0.4200
0.7000	73.8	742.2	0.1101	0.4364

Av. P. = 0.4283 $\pm$ 0.0077 mm.

Table 24

Partial Pressure of m-Dibromobenzene in a 9.937×10^{-2} M Solution in Decalin

Cu. ft. N_2	Temp., °F	Bar. Press., mm.	Dilution, g. to g.	O. D.	10^2P., mm.
0.4003	73.9	734.8	0.1643[a] - 5.507	0.362c	1.210
0.3999	74.7	734.8	0.1746[a] - 5.881	0.350	1.240
0.4000	75.7	734.8	0.1690[a] - 5.473	0.375	1.238
0.4001	76.8	743.8	0.1692[a] - 5.526	0.375	1.254

Av. P. = $(1.236 \pm 0.013) \times 10^{-2}$ mm.

[a] Grams of condensate.

Table 25

Partial Pressure of m-Dibromobenzene in a 1.014×10^{-2} M Solution in Decalin.

Cu. ft. N_2	Temp., °F	Bar. Press., mm.	Dilution, g. to. g.	O. D.	10^3P., mm.
2.5000	74.2	736.5	1.004[a] - 3.657	0.359	1.262
2.0000	70.8	740.9	0.7990[a] - 3.437	0.320	1.307
2.5090	73.5	740.9	1.026[a] - 4.563	0.304	1.324
1.7000	67.9	746.6	0.6931[a] - 3.308	0.282	1.308

Av. P. = $(1.300 \pm 0.019) \times 10^{-3}$ mm.

[a] Grams of condensate

Table 26

Partial Pressure of p-Dibromobenzene in a Saturated Solution in Decalin

Cu. ft. N_2	Temp., °F	Bar. Press., mm.	Dilution, g. to g.	O. D.	P., mm.
0.4998	77.4	739.6	0.1700[a] - 5.397 0.3170 - 3.831	0.342	0.1271
0.4000	77.3	739.6	0.1531[a] - 4.980 0.3852 - 3.795	0.385	0.1351
0.4999	77.4	739.6	0.1694[a] - 5.422 0.2828 - 3.718	0.358	0.1455
0.3000	76.7	741.0	0.1133[a] - 4.222 0.4133 - 3.592	0.380	0.1324
0.3000	77.4	741.0	0.1116[a] - 4.632 0.3231 - 3.728	0.269	0.1368
0.3000	78.0	741.0	0.1016[a] - 4.534 0.2469 - 3.681	0.200	0.1288
0.3000	78.7	738.0	0.1091[a] - 4.563 0.4144 - 3.664	0.332	0.1279
0.3001	78.8	738.0	0.1081[a] - 4.524 0.5292 - 3.814	0.413	0.1285
0.3000	78.9	738.0	0.1035[a] - 4.608 0.3399 - 3.773	0.272	0.1355
0.3000	78.9	738.0	0.1064[a] - 4.672 0.2637 - 3.604	0.228	0.1391

Av. P. = 0.1355 ± 0.0045 mm.

[a] Grams of condensate

Table 27

Partial Pressure of p-Dibromobenzene in a 1.061×10^{-2} M Solution in Decalin

Cu. ft. N_2	Temp., °F	Bar. Press., mm.	Dilution, g. to g.	O. D.	10^3 P., mm.
2.0000	76.4	743.1	0.7647 - 3.764	0.246	1.321
1.8000	72.9	737.3	0.6987 - 3.272	0.273	1.395
1.8000	73.7	737.3	0.6871 - 3.306	0.259	1.343
1.4000	74.4	737.3	0.5594 - 3.006	0.239	1.452
1.6000	76.9	734.3	0.6223 - 3.321	0.240	1.420

Av. P. = $(1.386 \pm 0.043) \times 10^{-3}$ mm.

Table 28

Partial Pressure of p-Dibromobenzene in a 3.211×10^{-2} M Solution in Decalin

Cu. ft. N_2	Temp. °F	Bar. Press., mm.	Dilution, g. to g.	O. D.	10^3 P., mm.
0.6000	78.8	740.6	0.2221[a] - 3.295	0.259c	4.075
0.6000	79.1	740.6	0.2219[a] - 3.239	0.262c	4.055
0.6000	75.0	745.0	0.2360[a] - 3.254	0.295	4.533
0.5001	74.9	745.0	0.1930[a] - 3.302	0.225	4.208
0.5000	74.8	745.0	0.1926[a] - 3.268	0.230	4.252

Av. P. = $(4.224 \pm 0.134) \times 10^{-3}$ mm.

[a] Grams of condensate

Table 29

Vapor Pressure of Nitrobenzene

Cu. ft. N_2	Temp., °F	Bar. Press., mm.	g. Cond.	P., mm.
2.9009	77.8	741.1	0.3225	0.5903
3.1023	78.4	739.9	0.3484	0.5981
2.9003	76.0	740.7	0.3259	0.5937
2.7005	73.6	743.0	0.3173	0.6178

Av. P. = 0.6000 $\pm$ 0.0089 mm.

Table 30

Partial Pressure of Nitrobenzene in a 3.462×10^{-2} M Solution in Decalin

Cu. ft. N_2	Temp., °F	Bar. Press., mm.	Dilution, g. to g.	O. D.	10^3 P., mm.
0.5998	74.9	738.2	0.2224[a] - 9.205 0.4806 - 3.594	0.294	2.992
0.6000	75.3	738.2	0.2132[a] - 9.283 0.8519 - 3.459	0.510	1.842
0.5000	75.3	738.2	0.1843[a] - 7.996 0.8855 - 3.626	0.520	3.022
0.4987	73.3	748.1	0.1813[a] - 8.766 0.6939 - 3.667	0.363	2.975
0.5002	75.0	745.1	0.1901[a] - 9.333 0.6234 - 3.687	0.310	3.031
0.4002	75.0	745.1	0.1463[a] - 8.591 0.7018 - 3.322	0.337	3.035

Av. P. = $(2.983 \pm 0.049) \times 10^{-3}$ mm.

[a] Grams of condensate.

Table 31

Partial Pressure of Nitrobenzene in a 3.409×10^{-4} M Solution in Decalin

Cu. ft. N_2	Temp., °F.	Bar. Press., mm.	Dilution, g. to g.	O. D.	10^4 P., mm.
0.6002	74.0	731.1	0.2037[a] - 5.724	0.329	2.771
0.6001	74.6	731.1	0.2117[a] - 5.561	0.354	2.907
0.6002	74.9	735.5	0.2174[a] - 5.209	0.360	2.770
0.6002	75.2	735.5	0.2211[a] - 5.366	0.370	2.933

Av. P. = $(2.845 \pm 0.075) \times 10^{-4}$ mm.

[a] Grams of condensate

Table 32

Partial Pressure of Nitrobenzene in a 1.150×10^{-3} M Solution in Decalin

Cu. ft. N_2	Temp., °F	Bar. Press., mm.	Dilution, g. to g.	O. D.	10^4 P., mm.
0.3998	76.9	735.2	0.1442[a] - 9.434	0.434	9.127
0.4000	77.3	735.2	0.1489[a] - 9.851	0.412	9.055
0.4000	77.4	735.2	0.1435[a] - 9.613	0.420	9.007
0.4002	77.2	735.2	0.1469[a] -10.02	0.395	8.824

Av. P. = $(9.003 \pm 0.090) \times 10^{-4}$ mm.

[a] Grams of condensate.

Table 33

Partial Pressure of m-Dinitrobenzene in a Saturated Solution in Decalin

Cu. ft. N_2	Temp., °F	Bar. Press., mm.	Dilution, g. to g.	O. D.	10^4 P., mm.
3.0000	74.4	740.1	1.2753[a] - 11.4253		
			1.293 - 3.3361	0.550	7.887
3.4000	83.8	738.2	1.3468[a] - 9.6738		
			0.3776 - 3.5573	0.199	8.026
3.1000	89.0	739.0	1.2232[a] - 14.2096		
			1.363 - 3.713	0.429	8.207
3.1391	84.5	738.9	1.2145[a] - 8.742		
			1.409 - 3.558		
			1.709 - 3.874	0.348	8.375
2.5998	76.2	740.0	1.0728[a] - 9.7097		
			1.5631 - 4.1175	0.558	8.050
2.5011	82.0	740.8	1.0255[a] - 10.030		
			0.8528 - 3.9408	0.301	8.357

Av. P. = $(8.150 \pm 0.163) \times 10^{-4}$ mm.

[a] Grams of condensate

Table 34

Partial Pressure of p-Dinitrobenzene in a Saturated Solution in Decalin

Cu. ft. N_2	Temp., °F	Bar. Press., mm.	Dilution, g. to g.	O. D.	10^4 P., mm.
2.5009	76.6	741.9	1.0106[a] - 9.7757 1.8845 - 3.5033	0.445	2.237
2.6016	74.2	739.8	1.0703[a] -10.495 1.9765 - 3.6184	0.434	2.200
2.5150	68.5	741.4	1.0488[a] - 8.7894 0.9018 - 3.6461	0.245	2.339
2.6998	70.1	744.0	1.1124[a] -10.241 1.8076 - 3.5816	0.432	2.207

Av. P. = $(2.246 \pm 0.047) \times 10^{-4}$ mm.

[a] Grams of condensate

Table 35

Vapor Pressure of Decalin

Cu. ft. N_2	Temp., °F	Bar. Press., mm.	g. Cond.	P., mm.
0.4001	77.7	742.4	0.1447	1.753
0.4000	78.4	742.4	0.1452	1.764
0.3998	78.8	742.4	0.1480	1.801
0.4001	79.8	741.8	0.1515	1.849
0.4241	79.6	741.8	0.1556	1.807
0.4000	79.6	741.8	0.1530	1.839
0.3999	79.4	741.8	0.1534	1.870

Av. P. = 1.811 ± 0.035 mm.

Table 36

Solubility of p-Dibromobenzene in Decalin at 35°C.

g. of Sat. Solution	Dilution, g. to g.	O. D.	Orig. Conc. M
0.8842	0.8842 - 3.848		
	0.2863 - 8.632		
	0.5845 - 3.745	0.310	0.9809
0.9533	0.9533 - 3.810		
	0.3333 - 8.425		
	0.4515 - 3.648	0.302	0.9280
0.9725	0.9725 - 3.928		
	0.3387 - 8.818		
	0.4948 - 3.609	0.356	1.028

Av. Conc. = 0.9790 ± 0.0340 M

Table 37

Solubility of m-Dinitrobenzene in Decalin at 35°C

g. of Sat. Solution	Dilution, g. to g.	O. D.	Orig. Conc., M
1.1524	1.1524 - 3.4856 0.1069 - 9.8382	0.500	2.681×10^{-2}
1.048	1.048 - 3.728 0.3505 - 3.723 0.2427 - 3.274	0.230	2.567×10^{-2}
1.109	1.109 - 3.736 0.5404 - 3.739 0.2602 - 3.661	0.408	2.576×10^{-2}
1.279	1.279 - 3.731 0.2915 - 3.718 0.3810 - 3.820	0.347	2.492×10^{-2}

Av. Conc. = $(2.579 \pm 0.051) \times 10^{-2}$ M

Table 38

Solubility of p-Dinitrobenzene in Decalin at 35°C

g. of Sat. Solution	Dilution, g. to g.	O. D.	Orig. Conc. M
1.6621	1.6621 - 3.6614 0.7128 - 8.7040 2.7358 - 8.7520	0.711	5.534×10^{-3}
2.438	2.438 - 3.621 0.4687 - 9.256 1.334 - 8.950	0.296	5.272×10^{-3}
2.528	2.528 - 3.689 0.7212 - 9.240 1.125 - 8.569	0.465	5.990×10^{-3}

Av. Conc. = $(5.600 \pm 0.261) \times 10^{-3}$ M

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VITA

Howard Wayne Haworth was born on October 6, 1931, in Philadelphia, Pennsylvania, the son of Margaret (née Tresler) and Wayne E. Haworth. After receiving his primary and secondary education at several locations and graduating in 1949, he enrolled at Emory University. He received a Bachelor of Arts degree in Chemistry in June, 1953. In June, 1953, he enrolled in the Graduate Division of the University of Alabama, where he received a Master of Science degree in Chemistry in June, 1955. He entered the Graduate Division of the Georgia Institute of Technology in September, 1955. While at the Georgia Institute of Technology, he served as an Instructor of Chemistry from 1956 to 1961. Grants to support his research were received from the Rayonier Corporation, the National Science Foundation, and the Alfred P. Sloan Foundation.

He married the former Phyllis H. Woodward in September, 1953, and has one child, Howard Wayne, Jr.